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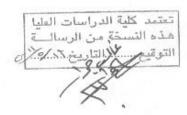
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Effect of Vanadium Addition on the Chemical Corrosion Resistance of Commercially Pure Aluminum Gozin Refined by Titanium at Different Temperatures

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توقع الطالب



# EFFECT OF VANADIUM ADDITION ON THE CHEMICAL CORROSION RESISTANCE OF COMMERCIALLY PURE ALUMINUM GRAIN REFINED BY TITANIUM AT DIFFERENT TEMPERATURES

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This Thesis was Submitted in Partial Fulfillment of the Requirements for the Degree of Master's in Chemical Engineering

Faculty of Graduate Studies University of Jordan

May, 2011

#### COMMITTEE DECISION

This Thesis/Dissertation (Effect of Vanadium Addition on the Chemical Corrosion Resistance of Commercially Pure Aluminum Grain Refined by Titanium at Different Temperatures) was Successfully Defended and Approved on May11<sup>th</sup> 2011

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#### **DEDICATION**

This thesis is dedicated to the memory of my father, Taysir Allawi, I am glad to know he saw this process through to its completion, offering the support to make it possible, as well as plenty of friendly encouragement.

To my mother whose love, patience, sacrifice, and support, make my education possible.

To my family through good times and bad, your kindness and extensive support have been ever present in this important time of my life, for which I am eternally grateful.

To all my friends for their continuous care and support.

#### **ACKNOWLEDGEMENT**

I would likely express my sincere gratitude to Dr. Ahmad Mohammad Abu-Yaghi and Dr. Adnan I. Zaid Al-Kilani for their splendid guidance, generous support and encouragement. I am very grateful for the knowledge they have shared with me and the guidance they have provided me throughout the development of this work. It has truly been an honor to work under their supervision.

Thanks are also to Sama Jordan Industrial Manufacture Company for their help in providing the teflon mould. Special thanks to Mr. Mohammad Arayda from Industrial Engineering laboratory in The University of Jordan for his help in the microscopic photographs.

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#### SYMBOLS AND ABBREVIATIONS

#### **Symbols**

CR Corrosion rate in (mg/mm<sup>2</sup>.yr) and in (mg/yr).

CR<sub>b</sub> Corrosion rate in blank solution (solution without inhibitor), (mg/mm<sup>2</sup>.yr).

 $\eta$  Corrosion inhibition efficiency.

CR<sub>wi</sub> Corrosion rate with inhibitor (mg/mm<sup>2</sup>.yr).

DCR Decrease in Corrosion Rate

M Molarity (mol/L).

A Surface area exposed to test in the corrosive medium (mm<sup>2</sup>).

t Time (yr).

 $\Delta W$  Weight loss (mg).

#### **Abbreviations**

Al Aluminum

MnAl Aluminum manganese.

Al<sub>2</sub>O<sub>3</sub> Aluminum oxide.

Al<sup>3+</sup> Aluminum ions.

Al(OH)<sup>-4</sup> Aluminate ions.

B Boron

Cl Chloride ions.

Cr Chromium.

Cu Cupper.

Hf Hafnium

HCl Hydrochloric acid.

HF Hydrofluoric acid.

H<sup>+</sup> Hydrogen ions.

OH Hydroxide ions.

H<sub>2</sub> Hydrogen molecules.

Mg(OH)<sub>2</sub> Magnesium hydroxide.

Mo Molybdenum.

Nb Niobium.

HNO<sub>3</sub> Nitric acid.

OM Optical Microscope.

PVC Polyvinyl Chloride.

K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Potassium dichromate.

Sc Scandium

SEM Scanning Electron Microscopy.

SiC Silicon carbide.

NaCl Sodium chloride.

NaF Sodium fluoride.

NaOH Sodium Hydroxide.

H<sub>2</sub>SO<sub>4</sub> Sulfuric acid.

Ta Tantalum

Ti Titanium

TiAl<sub>3</sub> Titanium aluminide.

W Tungsten.

V Vanadium.

H<sub>2</sub>O Water molecules.

XPS X-ray Photoelectron Spectroscopy.

Zr Zirconium.

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inhibitor at Different Temperatures

## EFFECT OF VANADIUM ADDITION ON THE CHEMICAL CORROSION RESISTANCE OF COMMERCIALLY PURE ALUMINUM GRAIN REFINED BY TITANIUM AT DIFFERENT TEMPERATURES

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#### **ABSTRACT**

Aluminum (Al) and its alloys solidify in a coarse columnar structure of large grain size. Thus aluminum is grain refined by different elements such as titanium (Ti) and titanium +boron (B), and this has been practiced since mid fifties to produce fine and homogeneous structure of aluminum alloys, and to enhance its mechanical properties and surface quality.

Although the effect of grain refiners on the metallurgical aspects and mechanical behavior have been previously investigated and reported in the literature, their effect on the corrosion behavior in the combination with the chemical environments and the operating conditions have been rarely investigated.

In this thesis, the effect of vanadium addition at different weight percentages on the chemical corrosion resistance of commercially pure aluminum grain refined by titanium in acidic and alkaline solutions with and without inhibitor at three different temperatures of  $25^{\circ}$ C,  $40^{\circ}$ C and  $60^{\circ}$ C, was investigated.

It was concluded that the increase in temperature resulted in an increase in the corrosion rate of pure aluminum grain refined by titanium at different weight percentages of vanadium both in 0.2 M hydrochloric acid (HCl) and 0.2 M sodium hydroxide (NaOH) solutions.

Also it was found that addition of vanadium at any percentage to commercially pure aluminum grain refined by titanium, resulted in an improvement of its corrosion resistance both in HCl and NaOH solutions at the three temperatures of 25 °C, 40 °C and 60 °C. The maximum improvement in hydrochloric acid was 76.75 % at 0.148 wt% V at 40 °C, and in sodium hydroxide was 40.29 % at 0.148 wt% V at 60 °C. These results are emphasized with

the general microstructure photograph of the corroded specimens in both solutions considered.

In the presence of 4 wt % sodium fluoride (NaF) as an inhibitor in the HCl solution and 3 wt % potassium dichromate ( $K_2Cr_2O_7$ ) in the NaOH solution resulted in enhancement of the corrosion resistance of commercially pure aluminum grain refined by titanium at different weight percentage of vanadium addition at the different investigated temperatures.

Finally it was found that the inhibition efficiency was increased by increasing the temperature for both HCl and NaOH solutions. The maximum increase of about 95.6 % was achieved at 0.005 wt% V at 40  $^{\circ}$ C by NaF in the HCl solution, and about 99.6 % for 0.236 wt % V at 40  $^{\circ}$ C by  $K_2Cr_2O_7$  in the NaOH solution.

#### **CHAPTER ONE: INTRODUCTION**

#### 1.1 Corrosion in General

Corrosion is the destructive attack of a metal by reaction with its environment. This attack may have many forms that depend on the metal involved, its size and shape, the atmospheric conditions, and the corrosion-producing agents present in it, (Ahmad, 2006). The most common forms found in machinery structures of corrosion are classified by the appearance of the corroded metal, such as: uniform attack, pitting and intergranular corrosion, (Fontana, 1987).

#### 1.2 Grain Refinement of Aluminum

Aluminum (Al) and most of its alloys solidify with a coarse columnar structure of large grain size in the absence of grain refiners, (Abdel Hamid, 1985), the disadvantage that lowers its strength, ductility and toughness. Thus, aluminum used in commercial applications is refined by small amounts of different elements such as titanium (Ti), titanium +boron (B), vanadium (V), zirconium (Zr) and molybdenum (Mo) to produce fine, homogeneous, an equiaxed grain structure of aluminum alloys within ingots or castings, and improves its mechanical properties and surface quality which results in greatly improved strength and hardness, (Abdel Hamid, 1989).

#### 1.3 Aluminum Properties and Uses

Aluminum is a very important metal in modern industry. It has many attractive properties, e.g. strength, light weight and when easily constructed material is required. This made its use in thousand applications such as in transportation, packaging, construction, and conductor cables, (Lide, 2007).

#### 1.4 Corrosion of Aluminum and Aluminum Micro-Alloys

Aluminum and its micro-alloys exhibit a wide range of corrosive attacks, varying from general etching of surface to penetrating attacks along the internal grain boundaries of the metal, (Eni, 2007). The corrosion products of aluminum are seen as white gray powdery deposits. The general microstructure of the grain boundaries of the aluminum micro-alloys can be observed and characterized by Optical Microscope (OM), which helps to examine and locate pits or intergranular corrosion in the micro-alloys.

In acidic media, i.e. hydrochloric acid (HCl), corrosion of aluminum and its micro- alloys proceed through a series of chemical reactions, characterized by evolution of hydrogen gas, as seen from the following overall main reaction:

$$Al + 3 H_3O^+ \longrightarrow Al^{3+} + 3 H_2O + 3/2 H_2\uparrow$$
 .....Eq.(1.1)

While in alkaline media, i.e. sodium hydroxide (NaOH), the corrosion reaction of aluminum and its micro- alloys characterized by a great amount of evolved hydrogen gas, the overall main reaction taking place is:

$$2\text{Al} + 2\text{OH}^{\text{-}} + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_{4}^{\text{-}} + 3\text{H}_2\uparrow \qquad \qquad \text{Eq.} (1.2)$$

#### **1.5 Corrosion Prevention**

Corrosion is present in different industries and prevention is the goal of these industries. Much has been done over the years to improve the corrosion resistance. Improvements include many techniques that aimed to reduce maintenance as well as improving reliability, (Roberge, 2008).

One of those techniques is inhibition; it is the practice in which corrosion is significantly retarded by adding small amounts of a reagent or substance that is capable to convert an active corrosion process into a passive process. Corrosion inhibitors are

selected on the basis of solubility or dispersibility in the fluids which are to be inhibited, (Ahmad, 2006).

In this research, sodium fluoride is used as an inhibitor in the acidic media. It reduces the corrosion rate to a great extent, and it reacts with aluminum in accordance with the following equation:

$$7H^{+}+Al_{2}O_{3}+F^{-}\rightarrow 2Al^{+3}+3H_{2}O+HF\uparrow.$$
 Eq.(1.3)

In the alkaline media the inhibition reagent is potassium dichromate. It decreases the corrosion rate in an excellent way, and it reacts with aluminum as in the following equation:

$$Al+Cr_2O_7^{-2}+7H_2O+3e^- \rightarrow Al(OH)_4^- +2Cr^{+3}+10 OH^-$$
 Eq.(1.4)

Although extensive research work has been carried out on grain refinement of aluminum and its alloys using different grain refiners e.g. Ti, Ti+B, Zr, Mo and V in the last 60 years, the effect of these grain refiners and the chemical environments and the operating conditions such as temperature on the corrosion resistance has been rarely investigated. In particular, the lack of information on the corrosion behavior of aluminum refined by vanadium formed the main objective of this study work.

#### 1.6 Objectives

The main objective of this study is to measure the corrosion rates of Al-Ti-V micro-alloys and compare them to that of commercially pure Al, in acidic (0.2 M HCl) and alkaline (0.2 M NaOH) solutions at different temperatures namely: 25, 40, and 60°C.

This study also aims at exploring the role of some available inhibitors on the corrosion rates of Al, and Al-Ti-V micro-alloys at these temperatures. Finally, make a physical characterization of the above mentioned micro-alloys to identify their microstructure, corrosion type and other related phenomena.

This thesis consists of six chapters, of which this introduction was the first. Literature survey of the previous works on the grain refinement of aluminum and its effect on the mechanical properties and corrosion resistance of aluminum are given in chapter two. The third chapter gives the theoretical background and general overview on corrosion in general, and on the corrosion of aluminum and aluminum micro-alloys in particular. Also, it covers common forms of corrosion that attacks aluminum, the different methods used to measure the corrosion rate, the factors influencing corrosion reactions, and how corrosion is prevented and controlled. The fourth chapter gives materials, equipment, and experimental procedures employed in this research work. The results obtained and their discussions are presented in the fifth chapter. The last chapter gives conclusions and recommendations for future work.

#### **CHAPTER TWO: LITREATURE SURVEY**

The literature on the grain refinement of aluminum is well presented and documented from the metallurgical and mechanical view points. However, little has been published on the chemical behavior of grain-refined aluminum.

Six decades ago, Clibula (1949) showed that the presence of titanium particularly in combination with carbon or boron produces a good refining effect in aluminum. This resulted in enhancement of mechanical behavior and surface quality. The Al cast industry has increasingly been adding Ti alone or with B, for this purpose.

Jones and Pearson (1976) reported that the ternary Al-Ti-B master alloy which contains 5% Ti and 1% B (by weight) is an effective grain refiner for aluminum, and is now widely used in aluminum industry and is commercially available. It has two crystalline inter-metallic compounds and large crystals of titanium aluminide (TiAl<sub>3</sub>), it is therefore expected that those two intermediate compounds in addition to the equiaxed fine structure will affect its corrosion resistance.

Abdel-Hamid (1985) found that aluminum and most of its alloys solidify with coarse columnar structure in the absence of grain refiners whereas fine and equiaxed grain structure is obtained by addition of small amounts of Ti or Ti+B into the melt before solidification. The effectiveness of various grain refining elements was investigated by Abdel-Hamid (1989). These included titanium (Ti), tantalum(Ta), zirconium (Zr), scandium (Sc), niobium (Nb), hafnium (Hf), vanadium (V), molybdenum (Mo), tungsten (W) and boron (B). Johnson et al (1993) reported that more than one mechanism is responsible for the grain refinement depending on the

nucleant (master alloy) used, the chemical composition of the alloy cast, and the processing conditions prevailing, e.g. contact time, and pouring temperature.

The criterion for the selection of an optimum grain refiner, such as the grain size required, the consistency of the quality of the cast products, and the lowest cost of grain refiner addition was studied by Mollard et al (1985) and Zaid (2001). The effect of addition of some alloying elements e.g. V, Mo, Zr and Ta on the fatigue strength and mode of failure of Al grain refined by either Ti or Ti+B are presented by Abdel-Hamid and Zaid (2000), Zaid and Al-Alami (2001) and Zaid and Al-Banna (2002).

Zaid and Abdel-Hamid (1999) investigated the effect of Zr and V addition to commercially pure Al refined with Ti and Ti+B, on the mechanical behavior, wear resistance, and mechanability. Improvements in hardness, mechanical strength and surface quality were achieved. Similarly the addition of Mo to the commercially pure Al refined by Ti resulted in improvement on its hardness, mechanical strength, mechanability, and surface quality at different cutting conditions, (Zaid and Hussein 2001).

Abeleke (2001) studied the corrosion behavior of four different types of aluminum alloys; two of them are reinforced with 20% by volume silicon carbide (SiC), while the remaining two are not reinforced. Weight loss, potentio-dynamic and cycle polarization technique were used to study their corrosion behavior in 3.5% wt. sodium chloride (NaCl) solution. The results showed that un-reinforced alloys have higher corrosion resistance as compared to their reinforced counterparts. The pits observed in all the alloys showed different shapes and structures.

The corrosion behavior of an iron–aluminum alloy and a composite of an iron–aluminum and steel were studied in sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution, (Masahashi et al 2006). They found that corrosion resistance deteriorates with increasing aluminum content of an iron–aluminum alloy. X-ray Photoelectron Spectroscopy (XPS) measurements showed a magnetite formation on the corroded surface and a preferential corrosion of iron. The corrosion resistance for the composite of an iron–aluminum alloy and chromium-molybdenum steel is comparable to that of chromium-molybdenum steel. This implies that a corrosion resistant composite is achievable by controlling the aluminum content of the iron–aluminum alloy without the additives.

Pardo et al (2008) investigated the corrosion behavior of commercial magnesium-aluminum alloys (AZ31, AZ80 and AZ91D) by electrochemical and gravimetric tests in 3.5 wt. % NaCl at 25°C. Corrosion products were analyzed by Scanning Electron Microscopy (SEM), energy dispersive X-ray analysis and low-angle X-ray diffraction. Corrosion damage was mainly caused by formation of a magnesium hydroxide (Mg(OH)<sub>2</sub>) corrosion layer. AZ80 and AZ91D alloys revealed the highest corrosion resistance. The relatively fine b-phase (Mg17A112) network and the aluminum enrichment produced on the corroded surface were the key factors limiting progression of the corrosion attack. Preferential attack was located at the matrix/b-phase and matrix/ aluminum manganese (MnAl) intermetallic compounds interfaces.

Liu et al (2008) examines the corrosion of aluminum- cupper alloys, containing up to 6.7% cupper (Cu) in 0.1M NaOH solution at 293 K. Enrichment of cupper beneath amorphous anodic films on relatively dilute, solid-solution Al–Cu alloys is

necessary before cupper can be oxidized and incorporated into the oxide layer. A similar enrichment arises during electro-polishing, which also develops an amorphous oxide. In these cases, external polarization is applied, usually generating a relatively high oxidation rate. Cupper is again found to enrich in the alloy, similarly to behavior with anodic polarization. However, following enrichment, discrete cupper-rich particles appear to be generated in the corrosion product. These are suggested to be nanoparticles of cupper, since the corrosion potentials of the alloys are low relative to that required for oxidation of copper. The corrosion rate increases with increase of both time and cupper content of the alloy, probably associated with a greater cathodic activity due to an increasing number of nano-particles. The corrosion proceeds with loss of aluminum species to the NaOH solution, but with retention of cupper in the layer of hydrated alumina corrosion product.

The influence of silicon carbide particles (SiCp) addition on the corrosion behavior of Al–Cu alloy (2014) was evaluated by Singh et al (2009) in 3.5% NaCl solution at 30°C using micro-structural and electrochemical measurements. Addition of 10 wt. % SiCp to the base alloy is found to increase its corrosion resistance considerably. Incorporation of SiCp beyond this proportion leads to an increase in corrosion rate of the synthesized composites. Addition of 25 wt. % SiCp to base alloy decreases corrosion resistances considerably. Micro-structural studies reveal the agglomeration of SiCp particles in the composites. This resulted in an increase of corrosion reaction with the increase of SiCp particles in the composites.

Recently, Zaid and Al-Theeb (2010) studied the effect of some grain refiners' addition (Ti, Zr, Ti+B) on the chemical corrosion resistance of commercially pure aluminum. They found that the addition of either Ti or Zr resulted in enhancement of Al corrosion resistance in some HCl solutions at 40 °C by 17.3 and 25.4%, respectively. Addition of Ti+B+Zr further enhanced the corrosion resistance by almost 160%. In the tested alkaline solutions, they have found that addition of either Ti or B reduced the Al corrosion resistance in NaOH by 10-15%. The effect of addition of Ti+Zr on corrosion resistance was dependent on NaOH concentration. A grain-refiner composed of Ti+B+Zr resulted only in slight enhancement (5%) of corrosion resistance.

#### CHAPTER THREE: THEORETICAL BACKGROUND

#### 3.1 Corrosion Overview

A wide spectrum of corrosion problems are encountered in industry as a result of combination of materials, environments and service conditions. Corrosion may not have a deleterious effect on a material immediately but it affects the strength, mechanical operations, physical appearance and it may lead to serious operational problems in future, (Ahmad, 2006). Corrosion may manifest itself as a cosmetic problem only, but it can also be very serious if deterioration of critical components is involved.

Corrosion is the primary mean by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals, (Roberge, 2006). Metals will also corrode when exposed to gaseous materials like acid vapors, formaldehyde gas, ammonia gas, and sulfur containing gases. Corrosion specifically refers to any process involving the deterioration or degradation of metal components.

The serious consequences of the corrosion process have become a problem of worldwide significance. In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expensive over-design. It can also jeopardize safety and inhibit technological progress (Roberge, 2008).

#### 3.2 Corrosion of Aluminum and Aluminum Micro Alloys

#### 3.2.1 General Scope on Aluminum and its Properties

Aluminum, as well as its micro-alloys, has been extensively applied in industry because of their particular properties such as low density, good appearance and corrosion resistance (Fontana, 1987).

Aluminum lies sufficiently far on the right side of the periodic table which indicates some hints of nonmetal behavior, reacting with hot alkalis to form aluminate ions (Al(OH)<sub>4</sub>) as well as the more typical metal reaction with acids to release hydrogen gas and form the positively charged metal ion, Al<sup>3+</sup>. In other words, aluminum is amphoteric; an amphoteric substance can either donate or accept a proton, (Polmear, 1995) and (Lide, 2007).

Aluminum is rare in its free form; its appearance is dull and its reactivity is passive by a film of aluminum oxide that naturally forms on the surface of the metal under normal conditions (Lide, 2007) and (Halvor, 2008), because of its strong affinity to oxygen. It is a strongly reactive metal that forms a high-energy chemical bond with oxygen. It occurs naturally in the form of bauxite, an ore containing aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), commonly called alumina, (Greenwood and Earnshaw, 1997) and (Guilbert et al, 1986). Some typical properties of aluminum are listed in table (3.1).

Table (3.1): Some typical properties of aluminum, (Halvor, 2008).

	71 1 1	, ,	,
Atomic Number	13	Melting Point	660.37 °C
Atomic weight	26.98154 g/mol	Boiling Point	2467 °C
Electron Configuration	2-8-3	Density at 293 K	$2.702 \text{ g/cm}^3$
Filling Orbital	3p1	Mean specific heat	0.219 cal/g .°C
Thermal conductivity	0.57 cal/cm.°C		

#### 3.2.2 Grain Refinement of Aluminum

Pure aluminum can be grain refined with small amounts of copper, magnesium, silicon, manganese, vanadium and other elements to impart a variety of useful properties such as increasing its resistance to corrosion, and surface finish, because it solidify with a coarse columnar structure of large grain size in the absence of grain refiners, (Abdel Hamid, 1985), and (Abdel Hamid, 1989).

Grain refinement is the set of specific techniques used in metallurgy to implement grain boundary and to ensure that the grains which make up a metallic object is sufficiently small. (Mollard et al, 1985) and (Zaid, 2001). The techniques and the corresponding mechanisms will vary based on what materials are being considered, (Johnson et al, 1993).

Vanadium enhances the grain refining efficiency of the aluminum micro alloy only when the V content is 0.1% or more, i.e., above the peritectic limit on the Al-V phase diagram (figure 3.1) (Abdel Hamid, 1989), vanadium proved that it improves the hardness, mechanical strength and surface quality of the aluminum alloy, (Zaid and Abdel-Hamid, 1999).

However; aluminum like other metals, has a disadvantage of being susceptible to different types of corrosion in the presence of aggressive anions (anions that have high electronegativity number, on the right side of the periodic table, such as chloride ions (Cl'), those anions have more tendency to attracts electrons towards it); aggressive anions will break down the oxide layer locally and start the pitting corrosion, which is a serious problem in industry. Therefore in the last six decades, numerous studies and research works were carried out on the corrosion behavior of aluminum and its microalloys aiming to overcome this problem and to improve their corrosion resistance hence

reducing the severe economical losses and other negative effects due to corrosion, (Ahmad, 2006).

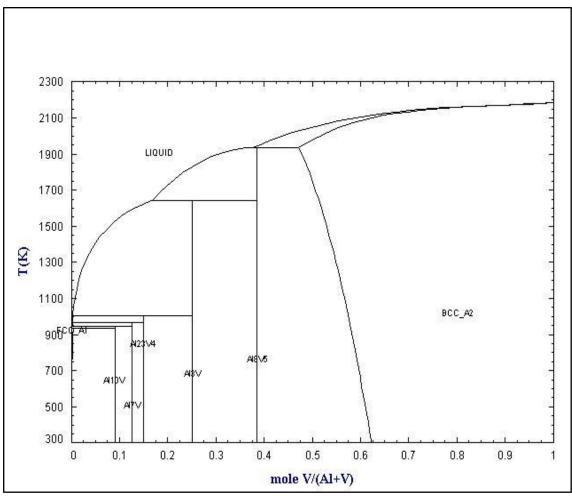


Figure (3.1): Aluminum-Vanadium phase diagram (Kostov and Friedrich, 2006).

### 3.2.3 Common Corrosion Forms and Attacks on Aluminum

Corrosion attack on aluminum surfaces is usually quite obvious since the products of corrosion are white and generally more voluminous than the original base metal, (Roberge, 2008) .It is evident as general etching, pitting, or roughness of the aluminum surfaces (Eni, 2007). However, at least two forms of attack on aluminum and its alloys are particularly serious:

### 1- The penetrating pit-type corrosion:

The most common effect of corrosion on aluminum alloys is pitting. It is caused primarily by variations in the grain structure between adjacent areas on the metal surfaces that are in contact with a corrosive environment, (Fontana, 1987) and (Ahmad, 2006).

Pitting is first noticeable as a white or gray powdery deposit, similar to dust, that blotches the surface. When the superficial deposit is cleaned away, tiny pits or holes can be seen on the surface. These pits may appear either as relatively shallow indentations or as deeper cavities of small diameters, (Roberge, 2008). Pitting may occur in any metal, but it is particularly in aluminum and its alloys, figure (3.2).

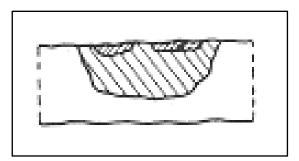


Figure (3.2): Pitting corrosion.

### 2- The intergranular attack:

The microstructure of metals and alloys is made up of grains, separated by grain boundaries. Intergranular corrosion is a localized attack along the grain boundaries, or immediately adjacent to grain boundaries, while the bulk of the grains remain largely unaffected, (Liu et al, 2005). It works inwards between the grains and causes more loss of strength than the same total destruction of metal uniformly distributed over the whole surface. This results in the loss of strength

and ductility, (Fontana, 1987). It is very common on stainless steel, nickel and aluminum alloys as indicated in figure (3.3).

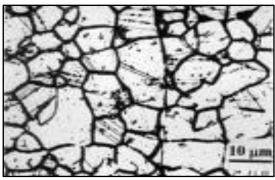


Figure (3.3): Intergranular Corrosion.

### 3.3 Dissolution and Corrosion Reactions of Aluminum

In most aqueous solutions, the dissolution reaction rate of aluminum is quite fast due to the oxide film which forms on its surface, (Drazic et al, 1983). The corrosion of aluminum occurs through an oxide film via ionic migration through the oxide film followed by dissolution at the oxide/electrolyte interface, (Ahmad, 2006).

Aluminum dissolution cannot be regarded as a single step process; the dissolution of aluminum involves two conjugated electron transfer reactions, one between aluminum (Al) and aluminum ions (Al $^{3+}$ ), and the other between water molecules (H $_2$ O) and hydrogen molecules (H $_2$ ), (Drazic et al., 1983) and (Greenwood and Earnshaw, 1997).

### 3.3.1 Dissolution and Corrosion Reaction of Aluminum in Acidic Medium

Aluminum and hydrochloric acid (HCl) react violently, creates heat and boil releasing steam. At the beginning of the reaction the impermeable protective oxide layer formed naturally on aluminum surface, must be dissolved by HCl, (Meixner, 2000) as follows:

$$Al_2O_3 + 6H_3O^+ \rightarrow 2Al^{3+} + 6H_2O$$
 .....Eq.(3.1)

This dissolution of the protective oxide layer, followed by the production of hydrogen and the overall main reaction taking place is:

$$A1 + 3 H_3O^+ \rightarrow A1^{3+} + 3 H_2O + 3/2 H_2\uparrow$$
.....Eq.(3.2)

### 3.3.2 Dissolution and Corrosion Reaction of Aluminum in Alkaline Medium

In solutions containing aggressive anions or in highly alkaline solutions, the dissolution procedure occurs in an easy way, it is quit fast which resulted in high hydrogen (H<sub>2</sub>) evolution, (Macdonald et al, 1999) and (Emregul and Abbas, 2000). First the reaction begins with the dissolution of the protective oxide film (hydration process at the film), and as a result, hydroxide ions (OH<sup>-</sup>) are formed:

$$2H_2O+2e^-\rightarrow H_2+2OH^-$$
 Eq.(3.3)

Then aluminum reacts with hydroxide ions in alkaline solution as:

$$Al+4OH^{-} \rightarrow Al(OH)_{4}^{-} + 3e^{-} \qquad Eq.(3.4)$$

And the overall main reaction taking place can be represented by the following equation:

$$2Al+2OH^{-}+6H_{2}O \rightarrow 2Al(OH)_{4}^{-}+3H_{2}\uparrow.$$
 Eq.(3.5)

### 3.4 Corrosion Mechanisms

Under the broad definition of corrosion as the deterioration of materials by reaction with the environment, the number of mechanisms whereby deterioration occurs is large. In general, a mechanism of corrosion is the actual atomic, molecular, or ionic transport process that takes place at the interface of a material. These processes usually

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involve more than one definable step, and the major interest is directed toward the slowest step that essentially controls the rate of the overall reaction. In corrosion this rate should be as slow as possible. Because these processes cannot be observed directly on an atomic scale, it is necessary to infer possible mechanisms from indirect measurements and observations. Examples are the rate of change in weight or dimensions, the rate of build up of corrosion products in the environment, changes in surface appearance examined by optical or electron microscopy, or changes in mechanical or physical properties, (Stansbury and Buchanan, 2000). In this study, the weight loss method is used for assessing corrosion rate.

### 3.4.1 Weight Loss Measurements

The weight loss technique involves exposing a specimen of material to a process environment for a given duration, then removing the specimen for analysis. The weight loss taking place over the period of exposure in the corrosive medium, being expressed as a corrosion rate according to the following expression:

$$CR = \frac{\Delta W}{tA} \qquad Eq. (3.6)$$

Or from the following expression:

$$CR = \frac{\Delta W}{t}.$$
 Eq. (3.7)

Where:

CR: The corrosion rate.

 $\Delta W$ : Weight loss (mg).

t: Time (yr).

A: Surface area exposed to test in the corrosive medium (mm<sup>2</sup>).

Noting that the corrosion rate, CR, in Eq. (3.6) is in (mg/.mm<sup>2</sup>.yr), and in Eq. (3.7) is in (mg/yr).

### 3.5 Factors Influencing Corrosion Reactions

As described in the previous sections, corrosion damage may take various forms which are themselves triggered by apparently different compounding factors. The initiation and progression of corrosion processes depend on the complex interaction of a multitude of factors such as:

### a- Temperature:

In most chemical reactions, an increase in temperature is accompanied by an increase in reaction rate. A well known rule-of-thumb suggests that the reaction rate doubles for each ten degree Celsius rise in temperature. Although this rule has many exceptions, it is important to take into consideration the influence of temperature when analyzing why materials fail. Other effects of temperature on corrosion systems may be exhibited through increasing ion diffusivity, decreasing gas solubility and decreasing electrolyte viscosity. Changing the temperature of an environment can significantly influence its corrosivity, (Fontana, 1987) and (Roberge, 2008).

#### b- Rate of flow of solution in contact with the metal:

Metals generally owe their corrosion resistance to a tightly adherent, protective film that builds up on the metal surface by corrosion processes. This film may consist of reaction products, adsorbed gases, or a combination of both of them. Any mechanical disturbance of this protective film can stimulate attack of the underlying metals until either the protective film is re-established, or the metal has been corroded away, (Fontana, 1987).

The mechanical disturbance itself can be caused by abrasion, impingement, turbulence, or cavitations. Under these conditions, which stimulate some corrosion of the metal surface, the effects of flow velocity may act to displace the corrosion products, thereby exposing fresh metal to the corrosion action of the solution. This action may lead to a much increased corrosion rate, (Roberge, 2008).

### c- Influence of oxygen in solution adjacent to the metal:

Dissolved oxygen has a major influence on corrosivity of metals, since oxygen is the principle reactant involved in the cathodic reaction and is involved in the passivation reactions that occur for most metals and alloys. In general the solubility of oxygen decreases as the temperature is increased. The effect of dissolved oxygen level on corrosion is dependent on the metal. For metals that form passive films like stainless steel and aluminum, high oxygen content is favorable as it helps to delay the initiation of pitting on the metal surface. Once pitting is initiated, the propagation rate is increased with high oxygen content, (Fontana, 1987) and (Baboian, 2005).

### d- Effect of pH:

The oxide layer which forms naturally on aluminum surface will deteriorate in environments with high or low pH, thus the initiation of corrosion in aluminum alloys is accelerated due to the attack of aluminum surface, (Baboian, 2005).

Moreover, the effect of pH is determined by the behavior of the metal oxide. Oxides of amphoteric metal e.g. Al, (it is oxide Al<sub>2</sub>O<sub>3</sub>), dissolve in both acid and alkaline media, where the metal will have its highest stability around the neutral pH level. Below a pH of 7.0 (acidic conditions) and above pH of 9.0 (alkaline conditions) there will normally be an increase in a corrosion rate of aluminum. Figure (3.4) shows the general effect of pH on the corrosion of aluminum, (Haven, 2008).

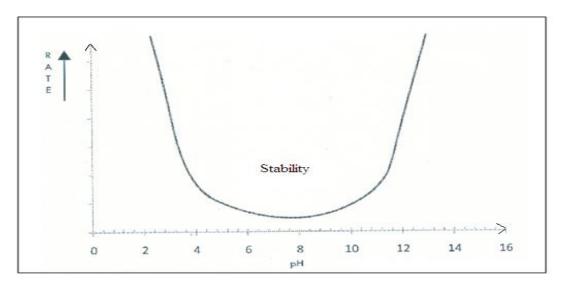


Figure (3.4): Effect of the pH on the corrosion of aluminum.

### 3.6 Corrosion Prevention

Extensive work has been carried out in the past to improve corrosion resistance and to protect from corrosion. Corrosion resistance can be improved or protected by one of the following methods:

- 1- Electrical protection (Cathodic and Anodic protection).
- 2- Addition of inhibitors.

### 3.6.1 Electrical Protection

- 1- Cathodic protection: The application of an external electric current to the metal so that it acts as a cathode and has no anodic areas on the same surface so its eliminated by transfer of electrons. After a sufficient current flow, the potential of anodic areas would become negative enough for corrosion to stop. Thus, the difference of potential between the cathodes and anodes on the structure decreases. Corrosion stops when potential of cathode becomes equal to the potential of anode. The anode would become more negative and the cathode more positive, (Ahmad, 2006).
- 2- Anodic protection: Is achieved by making the metal to be protected an anode in an electrolytic cell, the cell is supported by suitable potential from a power source. This causes the formation of a thick oxide layer on the metal surface in an appropriate electrolyte to form a metal oxide. This layer can resist and reduce the corrosion attack on a metal surface, (Fontana, 1987).

### 3.6.2 Addition of Inhibitors

Corrosion inhibitors are chemical compounds added to the corrosive medium in certain amounts to reduce the rate of its attack on the metal or alloy. The corrosion inhibition efficiency ( $\eta$  %) of corrosion inhibitor is a function of many factors, including but not limited to fluid composition, and flow regime. If the correct inhibitor

and quantity are selected properly, then it is possible to achieve high (90-99%) efficiency, (El-Etre, 2008).

The corrosion inhibition efficiency ( $\eta$  %) is defined as:

$$\eta\% = \frac{CR_b - CR_{wi}}{CR_b} \times 100\%$$
 Eq.(3.9)

Where:

CR<sub>b</sub>: The corrosion rate in blank solution (solution without inhibitor), (mg/mm<sup>2</sup>.yr).

CR<sub>wi</sub>: The corrosion rate with inhibitor (mg/mm<sup>2</sup>.yr).

### 3.7 Dissolution and Corrosion Reactions of Aluminum in Solutions Containing Inhibitors

### 3.7.1 Dissolution and Corrosion Reactions of Aluminum with Sodium Fluoride as an Inhibitor in Acidic Medium

Sodium fluoride (NaF) is an inorganic, colorless solid chemical compound. It is a source of the fluoride ion in diverse applications. Sodium fluoride is relatively inexpensive and has less hygroscopicity. Its ability to attract and hold water molecules from the surrounding environment is less than similar salts such as potassium fluoride, (Lewis, 1999).

Sodium fluoride is a strong ionizing compound, dissolving to give separated Na<sup>+</sup> and F<sup>-</sup> ions. It has been established that the presence of halide ions such as F<sup>-</sup> in the solution enhances the inhibition efficiency of most inhibitors. It is generally accepted that the halide ions facilitate adsorption of cations during metal corrosion by forming intermediate bridges between the metal surface and the positive end of the inhibitor. This may be attributed to the atomic radii, as well as the electronegativity, which

increase in respectively, in the halogen series (Umoren and Solomon, 2010). Equation (3.10) represents the reaction of sodium fluoride with aluminum oxide in acidic media:  $7H^{+}+Al_{2}O_{3}+F^{-}\rightarrow2Al^{+3}+3H_{2}O+HF\uparrow.....Eq.(3.10)$ 

### 3.7.2 Dissolution and Corrosion Reactions of Aluminum with Potassium Dichromate as an Inhibitor in Alkaline Medium

Potassium dichromate ( $K_2Cr_2O_7$ ) is a common inorganic chemical reagent; it is a crystalline ionic solid with a very bright, red-orange color most commonly used as an oxidizing agent in various laboratory and industrial applications, (Freeman, 2004).

As with all hexavalent chromium (Cr) compounds (chemical compounds that contain the element chromium in the +6 oxidation state), dissolve as stable complexes in water, transport easily, and adsorb on oxide surfaces. The octahedral, d3, trivalent compounds of Cr form very stable inert oxides;  $K_2Cr_2O_7$  is a mild oxidizer, (Kendig and Buchheit, 2003), the reaction between aluminum and  $K_2Cr_2O_7$  in alkaline media is given in the following equation:

$$Al + Cr_2O_7^{-2} + 7H_2O + 3e^- \rightarrow Al(OH)_4^- + 2Cr^{+3} + 10 OH^- ... Eq. (3.11)$$

# CHAPTER FOUR: MATERIALS, EQUIPMENT AND EXPERIMENTAL PROCEDURES

### 4.1 Materials

### 1- Specimens:

Commercially pure aluminum and five aluminum-titanium-vanadium (Al-Ti-V) micro alloys were use to accomplish this study. Chemical compositions of the tested aluminum micro alloys are listed in table (4.1). Commercially pure aluminum was used as the reference material. Commercially pure aluminum and its micro alloys were fabricated in wrought condition, and were manufactured by ingot casting process and provided A.I. Zaid.

Table (4.1): Aluminum and its different micro alloys, (weight %).

Specimen Number	Ti	V	Al
1	0	0	Remaining
2	0.15	0.005	Remaining
3	0.15	0.053	Remaining
4	0.15	0.112	Remaining
5	0.15	0.148	Remaining
6	0.15	0.236	Remaining

- 2- Distilled water.
- 3- Hydrochloric acid (HCl) stock solution.
- 4- Sodium hydroxide (NaOH) stock solution.
- 5- Sodium fluoride (NaF).
- 6- Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>).

### 4.2 Equipment and Lab Ware

- 1- Two water baths, (GFL 1083, Gemmyco YCW-010E)
- 2- Desiccator, (Chemical Engineering Laboratories).
- 3- Air Dryer, (Tzqnyu HD 1200).

- 4- Electronic Balance, (Shimadzu AUY 120, Error=1mg).
- 5- Fume hood, (Allen-Bradlfy).
- 6- Glassware: Flasks, beakers, pipettes.
- 7- Polyvinyl chloride (PVC) Teflon mould (Salameh, 2010), (figure 4.1), holders and stands.
- 8- Para film, soft brush and emery papers: 120, 240, 300, 400 and 600.
- 9- Optical Microscope (OM), (Industrial Engineering Department, supplied by MEIJI, type ML7100).

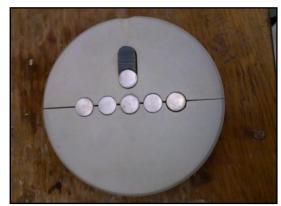


Figure (4.1): PVC Teflon mould with the specimens.

### 4.3 Experimental Procedures

### **4.3.1** Metallographic Test

### 4.3.1.1 Surface preparation for testing

In order to examine the metal microstructure, the specimens used are originally cut to a size appropriate for viewing with the microscope; they were first rough-smoothed by grinding. Depending on their size, specimens may be mounted in plastic or held in a clamp so they can be easily gripped for further preparation and examination. In this research the specimens were exposed to the following series of sample preparation.

### 1- Grinding:

Figure (4.2) shows the machine which was used for grinding purpose. It consists of a rotating disc covered with the emery paper of certain grit size. The velocity of the rotating disc can be changed by changing the motor speed to which it is connected. In addition a water stream is provided through a pipe, in order to act as a coolant to avoid temperature rise which may affect the microstructure of the specimen.



Figure (4.2): Grinding and polishing machine.

The emery papers used were classified into five grades of grit sizes: 120, 240, 300, 400 and 600, such that increasing the paper's number means decreasing the size of the grinding grains, i.e. causes finer and better surface quality. The following procedure was followed for metallurgical examination:

- a- Emery paper of grit120 was placed on the rotating, and fixed to it by the fixing frame.
- b- The required motor speed was adjusted, and then the machine was activated.
- c- The specimen was held against the rotating disc.
- d- The machine was switched off after scratches have been disappeared, then the surface grains kept in a unified direction.

e- The paper was changed using the finer grade (higher grit number) until all grades were finished. While turning from one grade to another grade, the specimen was rotated by 90° to get rid of the scratches which were generated from the previous grade.

### 2- Polishing:

In order to have a successful examination under the Optical Microscope (OM), polishing becomes as a subsequent action beyond grinding to generate a mirror-like surface, using the same that was used for grinding except that the emery papers are replaced by a polishing disc, covered with diamond paste of 1 micron size.

### 3- Etching and metallographic:

Here the specimens were emerged and etched in a 1.5% HCl, 2.5% nitric acid (HNO<sub>3</sub>) and 0.5 % hydrofluoric acid (HF) solution for 15 seconds, rinsed with water followed by acetone and dried.

### 4.3.1.2 Characterization and microstructure of the micro alloys

A photograph of the etched specimens were taken using an OM, figure (4.3), to reveal the constituents and general microstructure of the grain boundaries of the specimen.



Figure (4.3): The Optical Microscope.

#### **4.3.2** Gravimetric Measurements

Gravimetric measurements were performed using cylindrical specimens (table 4.1) of working area about 25 mm<sup>2</sup> immersed for 24 hours in 0.2 M HCl solution, with a pH of 0.69, and 0.2 M NaOH solution, with a pH of 13.3, with and without inhibitor at different temperatures (25, 40, 60 °C). All the experiments were carried out in a stand still conditions (no stirring). Prior to the tests, specimens were prepared by degreasing it in 1 % HCl solution at ambient conditions for two minutes to remove any protective or passive oxide layer, rinsing it with distilled water, keeping it in acetone for one minute, drying it using air dryer, and weighted to be ready for test.

Once the test was finished for each immersion time, the samples were extracted, rinsed with acetone, dried in hot air, kept in the desiccator for two hours, and then weighed again in order to calculate the weight gain per unit surface area.

The tests were performed in duplicate for each temperature, to guarantee the repeatability of the results within an accepted error range of 3%. The average weight loss was taken to calculate the corrosion rate at each temperature.

### 4.3.3 Characterization of Corrosion Products

After the tests, observations on the aluminum micro alloys using an OM apparatus were performed in order to examine and locate pits or intergranular corrosion.

### **CHAPTER FIVE: RESULTS AND DISCUSSION**

In this chapter, the results obtained throughout the experimental work of this thesis will be discussed under five main headings, these are:

- 1- Effect of vanadium addition to commercially pure aluminum grain refined by titanium on corrosion rate in HCl solution at different temperatures.
- 2- Effect of vanadium addition to commercially pure aluminum grain refined by titanium on corrosion rate in HCl in the presence of NaF as an inhibitor at different temperatures.
- 3- Effect of vanadium addition to commercially pure aluminum grain refined by titanium on corrosion rate in NaOH solution at different temperatures.
- 4- Effect of vanadium addition to commercially pure aluminum grain refined by titanium on corrosion rate in NaOH solution in the presence of  $K_2Cr_2O_7$  as an inhibitor at different temperatures.
- 5- Metallurgical examination of the general microstructure of the corroded surfaces in HCl and NaOH solutions.

The results in each of the above headings are presented graphically as corrosion rate vs. vanadium percentage, from 0 to 0.236 at a given solution temperature. The corrosion rate was calculated and expressed: either by (mg/mm².yr) or by (mg/yr), after immersion in appropriate solutions for 24 hours and determining the differences in the weight of the specimens before and after the immersion. It is worth noting the advantage of presenting the corrosion rate once in (mg/mm².yr) and in (mg/yr) to assist in comparing the effect of V addition in both wear resistance and corrosion resistance.

## 5.1 Effect of Vanadium Addition to Commercially Pure Aluminum Grain Refined by Titanium on Corrosion Rate in HCl Solution at Different Temperatures

Vanadium is added to commercially pure aluminum as a grain refiner resulting in small grain size and improvement in its mechanical behavior and wear resistance, (Zaid and Abdel-Hamid, 1999).

Figure (5.1) shows the effect of vanadium addition on the corrosion rate of commercially pure aluminum grain refined by Ti, (Al-0.15 % Ti). It can be seen from this figure and figure (5.2) that except at infinitesimally small percentage of vanadium addition less than 0.05 resulted in an increase in corrosion rate.

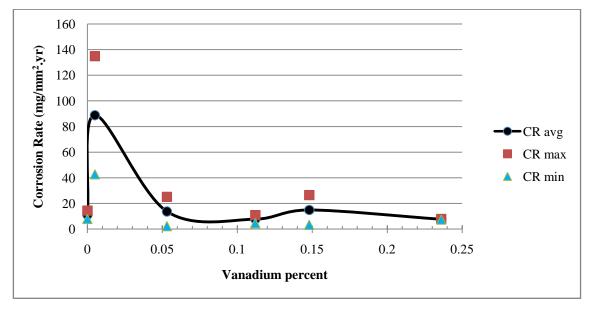


Figure (5.1): Corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M HCl solution at 25°C.

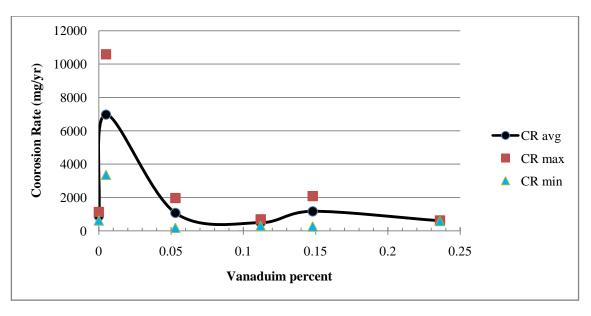


Figure (5.2): Corrosion rate (mg/ yr) vs. vanadium percent in the specimen in 0.2 M HCl solution at 25°C.

Increasing the temperature of the HCl solution e.g. to 40 °C and 60 °C resulted in higher rate of corrosion. However, corrosion rate still decreases with vanadium addition at all temperatures. The maximum reduction in corrosion rate was approximately 30 % at 0.112 wt % vanadium addition, and the minimum reduction was approximately at 25 °C. Similarly, at higher temperatures, 40 °C, (figures 5.3 and 5.4), and 60 °C, (figures 5.5 and 5.6), the trend remained the same but addition of vanadium becomes more effective as the temperature of the HCl solution is increased.

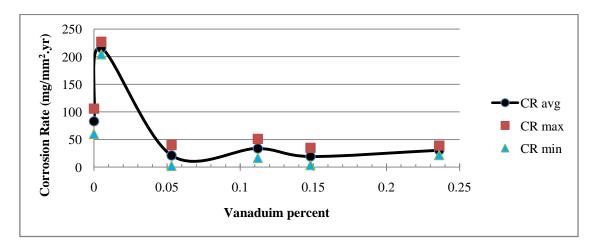


Figure (5.3): Corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M HCl solution at 40°C.

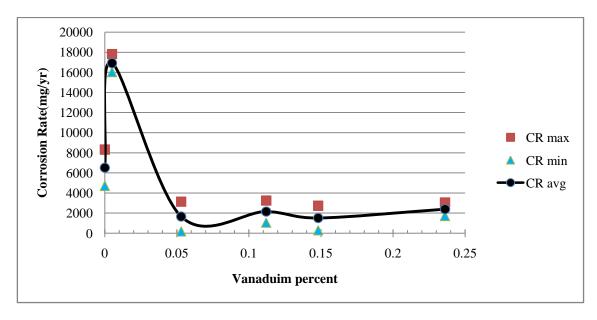


Figure (5.4): Corrosion rate (mg/yr) vs. vanadium percent in the specimen in 0.2 M HCl solution at 40°C.

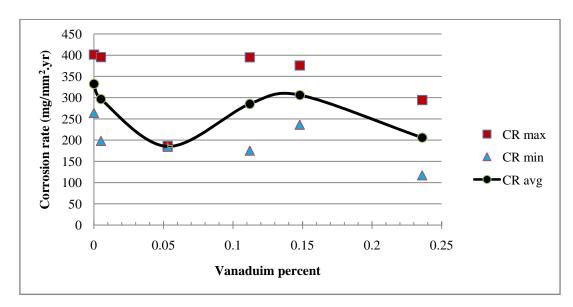


Figure (5.5): Corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M HCl solution at 60°C.

The maximum reduction in corrosion rate was approximately 77% at 0.148 wt % vanadium addition, and the minimum was approximately 60 % at 0.112 wt % vanadium addition at 40 °C. While the maximum reduction in the corrosion rate was approximately 44 % at 0.053 wt % vanadium addition, and the minimum was approximately 7 % at 0.148 wt % vanadium addition at 60 °C.

In the previous figures the scatter of data is obvious, and in the last one it is about  $\pm$  30 %, this can be explained by the existence of the different intermetallic compounds within the aluminum matrix, such as: TiAl<sub>3</sub> and Al<sub>2</sub>V<sub>5</sub>, (Kostov and Friedrich, 2006).

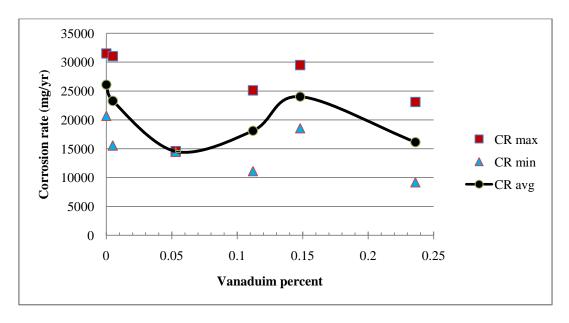


Figure (5.6): Corrosion rate (mg/yr) vs. vanadium percent in the specimen in 0.2 M HCl solution at 60°C.

It is interesting to note that the maximum decrease in corrosion rate is around the peritectic point (0.1 wt% vanadium addition on the Al-V phase diagram, as shown in figure(3.1), this is the wt% addition which is normally used in industrial applications), (Zaid and Abdel-Hamid, 1999).

Figures (5.7) and (5.8) give a comparison of the effects of different V wt% addition on the corrosion rate of commercially pure Al grain refined by Ti at the three temperatures of 25, 40 and 60 °C. The maximum reduction in the corrosion rate was approximately 77% at 0.148 wt % addition of V at 40 °C, and the minimum was approximately 7 % at 0.148 wt % addition of V at 60 °C. This may be explained in

terms of the increase in the number of grains due to the refining effect and the activation energy of the corrosive media as follows:

- 1- Increasing the number of grains per unit area will cause more intergranular boundaries (surface area) exposed to the corrosive medium, this resulting in increasing the corrosion rate.
- 2- Increasing the temperature increases the activation energy of the corrosive media, thus promoting more attack on the solid surface through increasing the diffusivity of hydrogen ions towards the aluminum surface. This effect is being more pronounced in the case of 60 °C.

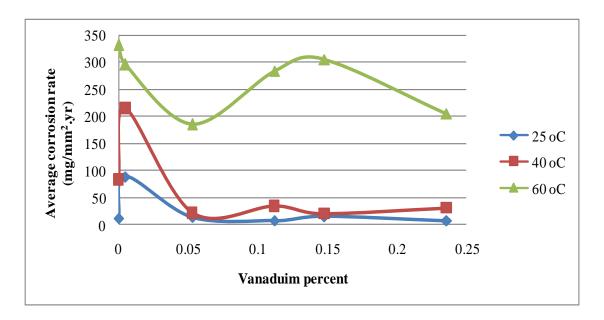


Figure (5.7): Average corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M HCl solution at 25, 40 and 60°C.

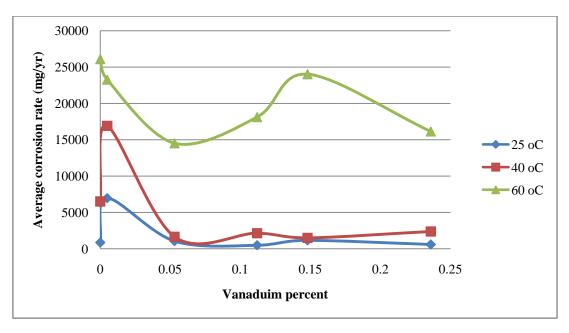


Figure (5.8): Average corrosion rate (mg/yr) vs. vanadium percent in the specimen in 0.2 M HCl solution at 25, 40 and 60°C.

The exact values of the corrosion rate in (mg/yr) and in (mg/mm<sup>2</sup>.yr) at the three temperatures are explicitly given in the tables of Appendix B1.

### 5.2 Effect of Vanadium Addition to Commercially Pure Aluminum Grain Refined by Titanium on the Corrosion Rate in HCl Solution in the Presence of NaF as an Inhibitor at Different Temperatures

It can be seen from figures (5.9) and (5.10) that the addition of V at any percentage to commercially pure Al grain refined by Ti resulted in decrease in its corrosion rate in HCl solution in the presence of NaF at temperature of 25 °C. The maximum decrease in corrosion rate is 66 % at this temperature at 0.112 wt % V addition. This may be due to the adsorption of NaF on the Al surface.

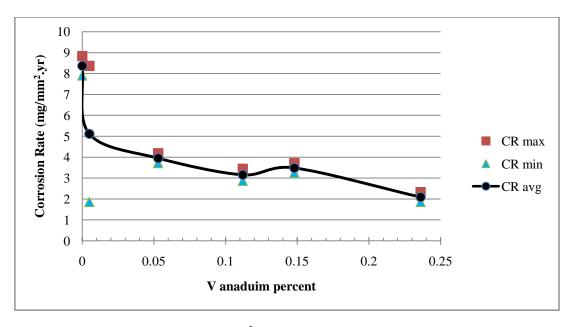


Figure (5.9): Corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M HCl solution with 4 wt % NaF at 25°C.

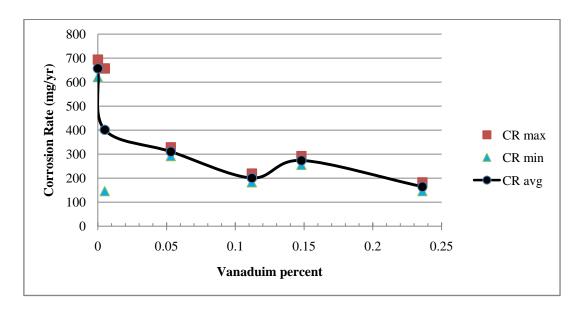


Figure (5.10): Corrosion rate (mg/ yr) vs. vanadium percent in the specimen in 0.2 M HCl solution with 4 wt % NaF at 25°C.

Similar trend was noted for the different V addition percentage in the same solution at 40  $^{\circ}$ C, (figures 5.11 and 5.12), and at 60  $^{\circ}$ C, (figures 5.13 and 5.14).

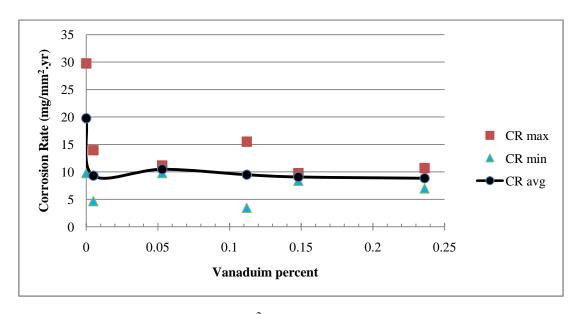


Figure (5.11): Corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M HCl solution with 4 wt % NaF at 40°C.

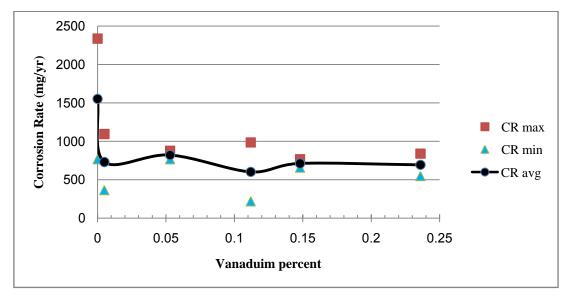


Figure (5.12): Corrosion rate (mg/ yr) vs. vanadium percent in the specimen in 0.2 M HCl solution with 4 wt % NaF at 40°C.

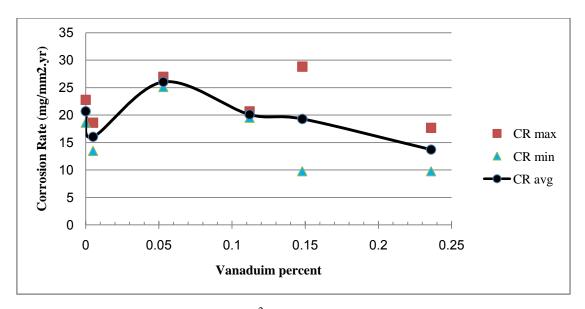


Figure (5.13): Corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M HCl solution with 4 wt % NaF at 60°C.

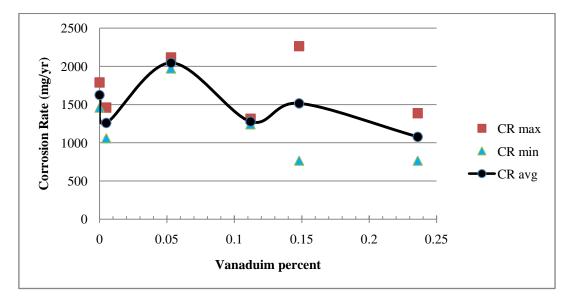


Figure (5.14): Corrosion rate (mg/ yr) vs. vanadium percent in the specimen in 0.2 M HCl solution with 4 wt % NaF at 60°C.

As the temperature increased the corrosion rate increased but remains less than it in the case of blank HCl solution. Furthermore, it can be seen from figures (5.15) and (5.16) that the effect of adding NaF to the HCl solution improved the corrosion resistance of the solution. This improvement increased with increase of temperature reaching about 90 % for commercially pure Al.

It can be also seen that about 95 % in the case of addition of different levels of V as explicitly shown in the tables of Appendix B2. Since as the temperature increased, the adsorption of NaF on the Al surface increased causes the corrosion rate to decrease and the inhibition efficiency to increase, as presented in tables (5.1), (5.2) and (5.3).

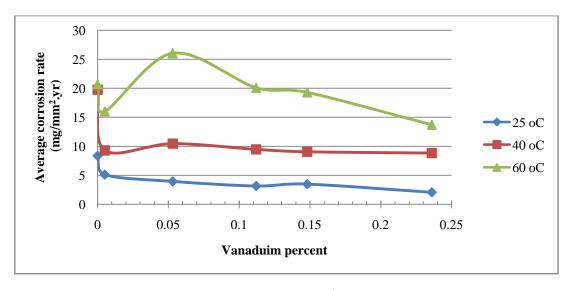


Figure (5.15): Average corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M HCl solution with 4 wt % NaF at 25, 40 and 60°C.

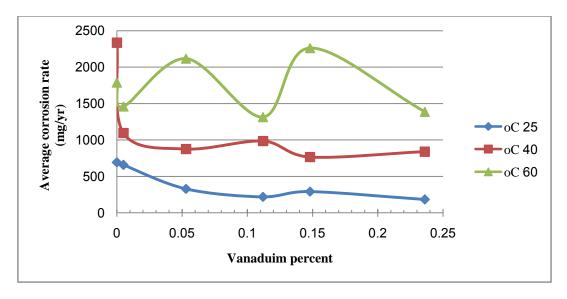


Figure (5.16): Average corrosion rate (mg/ yr) vs. vanadium percent in the specimen in 0.2 M HCl solution with 4 wt % NaF at 25, 40 and 60°C.

Table (5.1): Effect of V addition on the inhibition efficiency in HCl solution at 25 °C.

V%	$CR_b (mg/mm^2.yr)$	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr)	η%
0	11.16	8.37	25.00
0.005	88.81	5.11	94.24
0.053	13.72	3.95	71.19
0.112	7.75	3.16	59.26
0.148	14.88	3.49	76.56
0.236	7.67	2.09	72.73

Table (5.2): Effect of V addition on the inhibition efficiency in HCl solution at 40 °C.

V%	$CR_b(mg/mm^2.yr)$	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr)	η%
0	83.00	19.76	76.19
0.005	215.51	9.30	95.69
0.053	21.16	10.46	50.55
0.112	33.87	9.47	72.03
0.148	19.30	9.07	53.01
0.236	30.46	8.83	70.99

Table (5.3): Effect of V addition on the inhibition efficiency in HCl solution at 60 °C.

V%	CR <sub>b</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr)	η%
0	332.46	20.69	93.78
0.005	296.65	16.04	94.59
0.053	185.06	26.04	85.93
0.112	285.01	20.09	92.95
0.148	305.95	19.30	93.69
0.236	205.75	13.72	93.33

Comparison between the corrosion rate of commercially pure Al grain refined by Ti in (mg/mm<sup>2</sup>.yr) in the HCl in presence of NaF at different V addition percentage at 25, 40 and 60 °C are shown in figures (5.17), (5.18) and (5.19) respectively. It is well noted that the addition of NaF as an inhibitor causes the corrosion rate to decrease at any V addition percentage at the given temperatures.

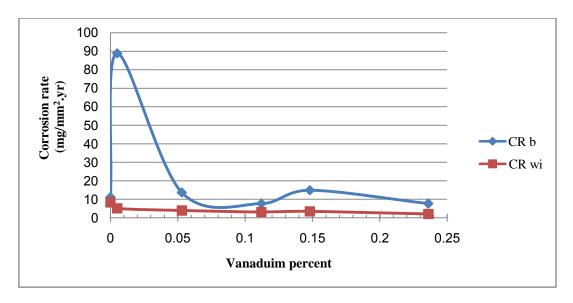


Figure (5.17): Average corrosion rate (mg/mm $^2$ .yr) vs. vanadium percent in the specimen in Blank 0.2 M HCl solution and in 0.2 M HCl solution with 4 wt % NaF at  $25^{\circ}$ C.

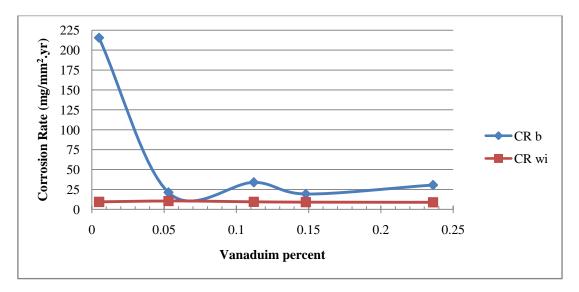


Figure (5.18): Average corrosion rate (mg/mm $^2$ .yr) vs. vanadium percent in the specimen in blank 0.2 M HCl solution and in 0.2 M HCl solution with 4 wt % NaF at  $40^{\circ}$ C.

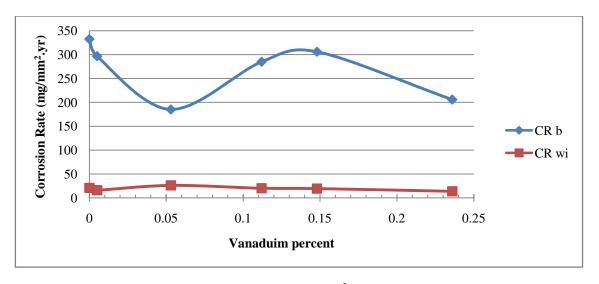


Figure (5.19): Average corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in Blank 0.2 M HCl solution and in 0.2 M HCl solution with 4 wt % NaF at 60°C.

# 5.3 Effect of Vanadium Addition to Commercially Pure Aluminum Grain Refined by Titanium on Corrosion Rate in NaOH Solution at Different Temperatures

Figures (5.20) and (5.21) show the effect of addition of V, at different addition percentage to commercially pure Al grain refined by Ti on its corrosion rate in NaOH solution at 25 °C. It can be seen from these two figures that the addition of V to commercially pure Al at any percentage resulted pronouncly in improving its corrosion resistance. The maximum decrease in corrosion rate of 37.78 % and the minimum of 11.11 % were achieved at 0.053 and 0.148 wt % V addition respectively at 25 °C.

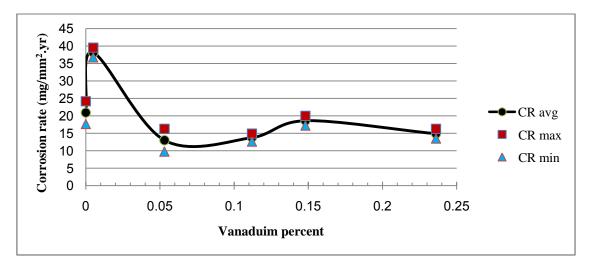


Figure (5.20): Corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution at 25°C.

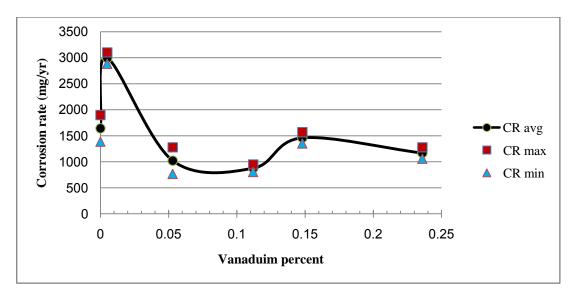


Figure (5.21): Corrosion rate (mg/yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution at 25°C.

As in the case of HCl solution and as expected increasing the temperature of the NaOH solution resulted in increases of the corrosion rate, i.e. decreases in the corrosion resistance at the same percentage of the V addition, as shown in figures (5.22), (5.23), (5.24) and (5.25).

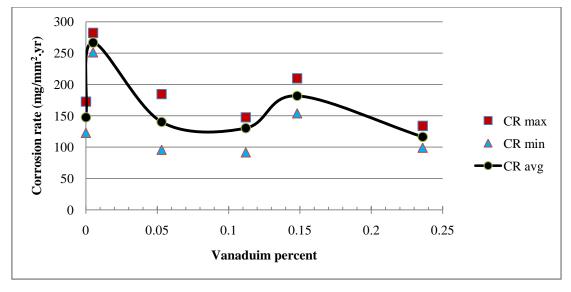


Figure (5.22): Corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution at 40°C.

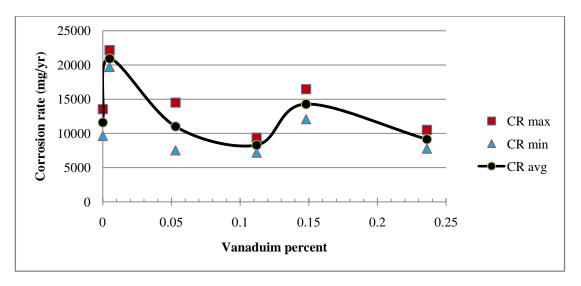


Figure (5.23): Corrosion rate (mg/yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution at 40°C.

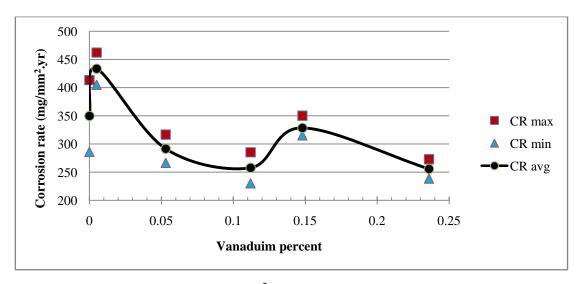


Figure (5.24): Corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution at 60°C.

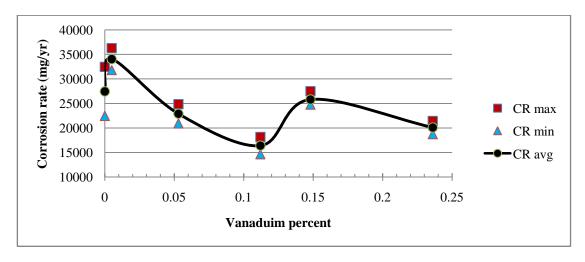


Figure (5.25): Corrosion rate (mg/yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution at 60°C.

The maximum reduction in the corrosion rate was approximately 28 % at 0.112 wt % V addition, and the minimum reduction was approximately 5% at 0.053 wt % V additions at 40  $^{\circ}$ C. Whereas the maximum reduction in the corrosion rate was approximately 40 % at 0.112 wt % V addition, and the minimum reduction was approximately 6 % at 0.148 wt % V addition at 60  $^{\circ}$ C.

Figures (5.26) and (5.27) show the corrosion rate of commercially pure Al grain refined by Ti in the NaOH solution at different V addition percentage at 25, 40 and 60 °C. The maximum reduction in the corrosion rate was approximately 40% at 0.112 wt % V addition at 40 °C, and the minimum reduction was approximately 5% at 0.053 wt % V addition at 40 °C as explicitly shown in the tables of Appendix B3.

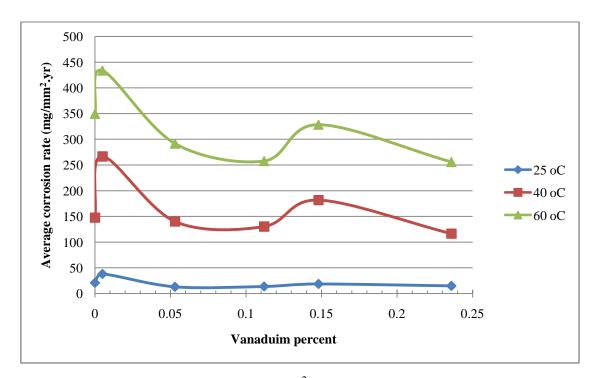


Figure (5.26): Average corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution at 25, 40, and 60°C.

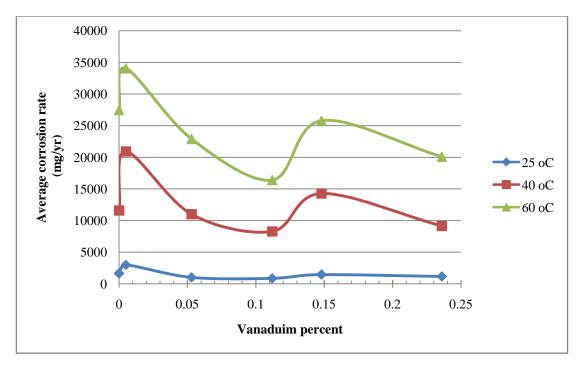


Figure (5.27): Average corrosion rate (mg/yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution at 25, 40 and 60°C.

# 5.4 Effect of Vanadium Addition to Commercially Pure Aluminum Grain Refined by Titanium on the Corrosion Rate in NaOH Solution in the Presence of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as an Inhibitor at Different Temperatures

The addition of V at different weight percentage to commercially pure Al grain refined by Ti on its corrosion rate in NaOH solution in the presence of  $K_2Cr_2O_7$  as an inhibitor is shown in figures (5.28) and (5.29) at 25 °C. It can be seen from these figures that the corrosion rate increases as the V percent increases, but remained much less than the corrosion rate, at each V percent, in the absence of the  $K_2Cr_2O_7$  inhibitor.

On the whole, it can be seen that the presence of  $K_2Cr_2O_7$  as an inhibitor caused reduction in the corrosion rate, i.e. increase in corrosion resistance at all rates of V addition as compared to the blank NaOH solution, at 25  $^{\circ}$ C, without inhibitor. This effect is due to adsorption of  $K_2Cr_2O_7$  inhibitor on the Al surfaces.

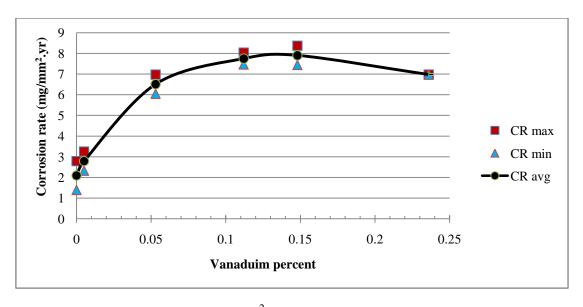


Figure (5.28): Corrosion rate (mg/mm $^2$ .yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution with 3 wt %  $K_2Cr_2O_7$  at  $25^{\circ}C$ .

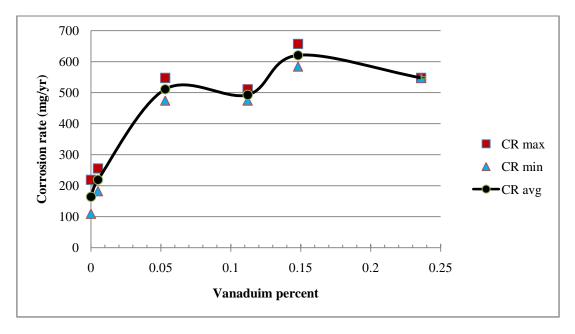


Figure (5.29): Corrosion rate (mg/ yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution with 3 wt %  $K_2Cr_2O_7$  at  $25^{\circ}C$ .

Raising the temperature of the solution to 40 °C resulted in decrease of corrosion rate with increase of V addition levels, as shown in figures (5.30) and (5.31), whereas the corrosion rate increased for commercially pure Al.

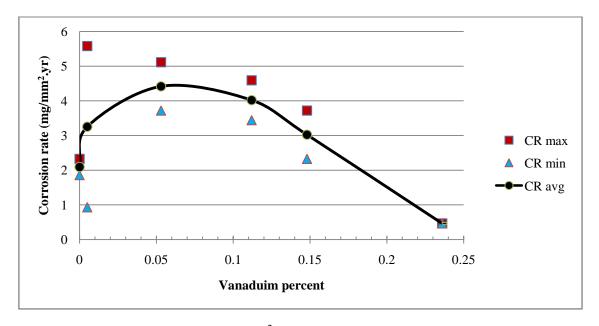


Figure (5.30): Corrosion rate (mg/mm $^2$ .yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution with 3 wt %  $K_2Cr_2O_7$  at  $40^{\circ}C$ .

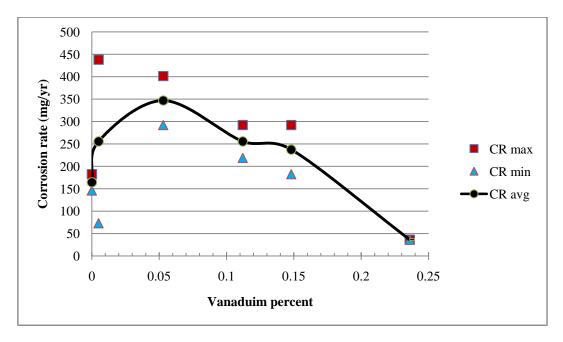


Figure (5.31): Corrosion rate (mg/ yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution with 3 wt %  $K_2Cr_2O_7$ at  $40^{\circ}C$ .

Furthermore, raising the temperature to  $60\,^{\circ}\text{C}$  caused reduction in the corrosion rate with increase of V addition levels, as shown in figures (5.32) and (5.33).

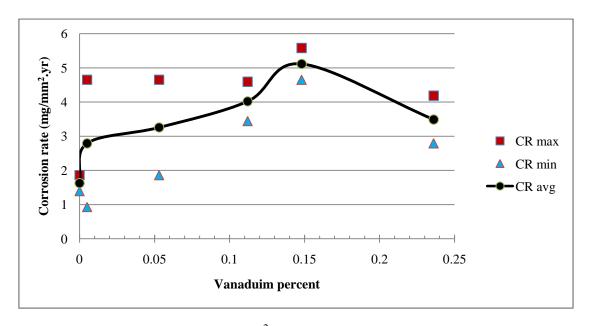


Figure (5.32): Corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution with 3 wt %  $K_2Cr_2O_7$  at  $60^{\circ}C$ .

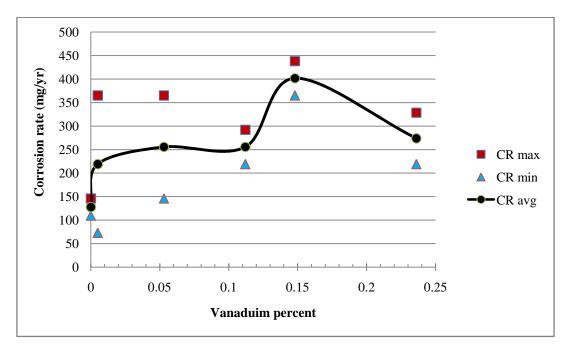


Figure (5.33): Corrosion rate (mg/ yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution with 3 wt %  $K_2Cr_2O_7$  at  $60^{\circ}C$ .

Figures (5.34) and (5.35) show that increasing the temperature results in a decrease in the corrosion rate of commercially pure Al grain refined by Ti in the NaOH solution in the presence of  $K_2Cr_2O_7$  at different V addition percentage. And as the temperature increased, the efficiency of  $K_2Cr_2O_7$  increased; this can be explained due to an increase of adsorption of  $K_2Cr_2O_7$  on Al surface.

The effect of V addition on the inhibition efficiency is shown in tables (5.4), (5.5) and (5.6) at 25, 40 and 60 °C respectively. It can be seen from the result in these tables that the presence of  $K_2Cr_2O_7$  as an inhibitor in NaOH solution improved the inhibition efficiency of the solution, reaching about 99.5 % for commercially pure Al and about 99 % in case of addition of different levels of V as explicitly shown in the tables of Appendix B4.

Table (5.4): Effect of V addition on the inhibition efficiency in NaOH solution at 25 °C.

V%	CR <sub>b</sub> (mg/mm <sup>2</sup> .yr)	$CR_{wi}(mg.mm^2.yr)$	η%
0	20.92	2.09	90.00
0.005	38.13	2.79	92.68
0.053	13.02	6.51	50.00
0.112	13.78	7.75	43.75
0.148	18.60	7.90	57.50
0.236	14.88	6.97	53.12

Table (5.5): Effect of V addition on the inhibition efficiency in NaOH solution at 40 °C.

V%	CR <sub>b</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr)	η%
0	147.63	2.09	98.58
0.005	266.66	3.25	98.78
0.053	140.19	4.42	96.85
0.112	130.31	4.02	96.92
0.148	181.80	3.02	98.34
0.236	116.48	0.46	99.60

` ,		-	,
V%	CR <sub>b</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr)	η%
0	349.66	1.63	99.53
0.005	433.59	2.79	99.36
0.053	291.54	3.25	98.88
0.112	257.74	4.02	98.44
0.148	328.50	5.11	98.44
0.236	255.73	3.49	98.64

Table (5.6): Effect of V addition on the inhibition efficiency in NaOH solution at 60 °C.

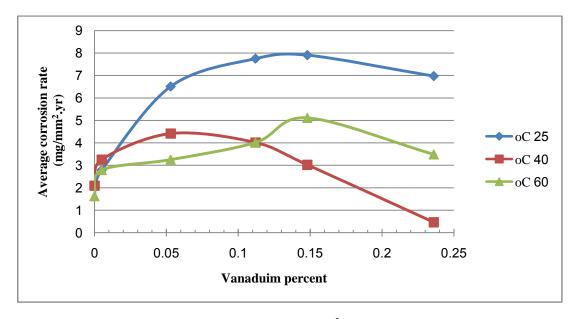


Figure (5.34): Average corrosion rate (mg/mm $^2$ .yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution with 3 wt %  $K_2Cr_2O_7$  at 25, 40 and 60 $^{\circ}C$ .

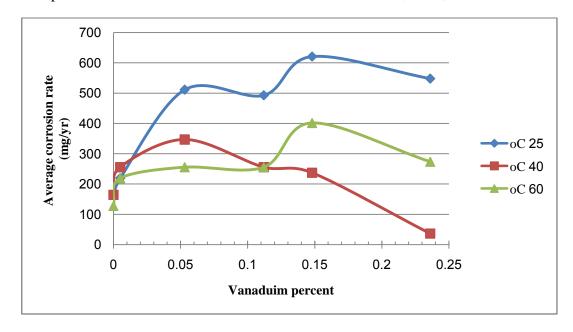


Figure (5.35): Average corrosion rate (mg/yr) vs. vanadium percent in the specimen in 0.2 M NaOH solution with 3 wt %  $K_2Cr_2O_7$  at 25, 40 and  $60^{\circ}C$ .

Figures (5.36), (5.37) and (5.38) shows the average corrosion rate vs. V percent at temperatures of 25, 40 and 60  $^{\circ}$ C respectively in the blank case and in the presence of  $K_2Cr_2O_7$  inhibitor for comparison purposes.

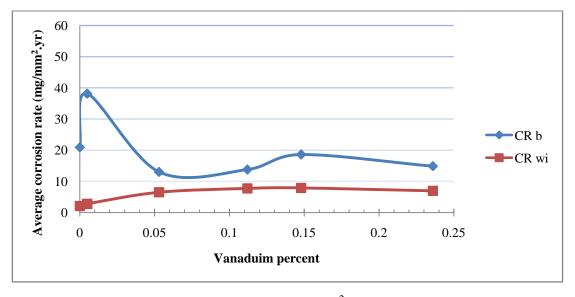


Figure (5.36): Average corrosion rate (mg/mm $^2$ .yr) vs. vanadium percent in the specimen in blank 0.2 M NaOH solution and in 0.2 M NaOH solution with 3 wt %  $K_2Cr_2O_7$  at 25 $^\circ$ C.

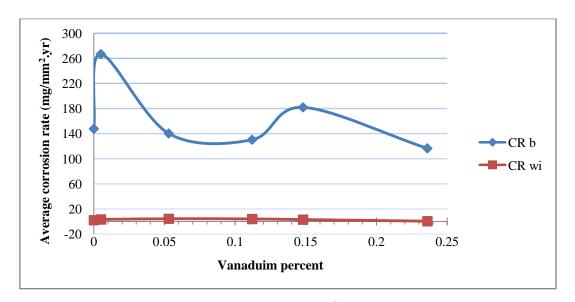


Figure (5.37): Average corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in blank 0.2 M NaOH solution and in 0.2 M NaOH solution with 3 wt %  $K_2Cr_2O_7$  at  $40^{\circ}C$ .

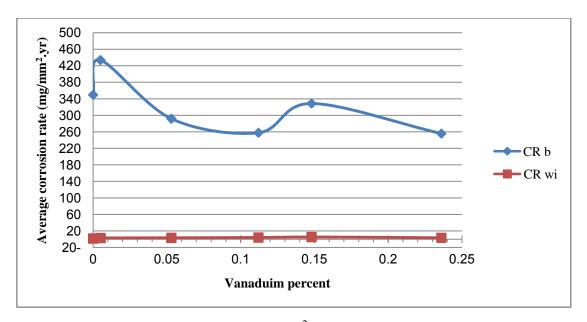


Figure (5.38): Average corrosion rate (mg/mm<sup>2</sup>.yr) vs. vanadium percent in the specimen in blank 0.2 M NaOH solution and in 0.2 M NaOH solution with 3 wt % K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at 60°C.

Comparing of all the figures in HCl and NaOH solutions without and with inhibitor, scatter of data in the inhibited solution is less than that in the uninhibited solution; this can be interpreted due to the adsorption of the inhibitor on the aluminum surface, which in turn reduces the corrosion rate.

## 5.5 Metallurgical Examination of the General Microstructure of the Corroded Surfaces in HCl and NaOH Solutions

Figure (5.39) is a photograph of the original microstructure of commercially pure Al at magnification of X400.

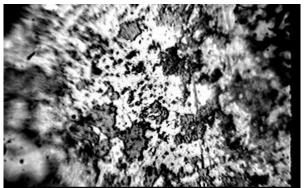


Figure (5.39): Microstructure of commercially pure aluminum at magnification of X400.

Figure (5.40) is a photograph showing the microstructure of commercially pure Al after an exposure of 24 hrs to 0.2 M HCl solution at 60°C at magnification of X400, resulted in pitting and wiping off the grains and their boundaries.

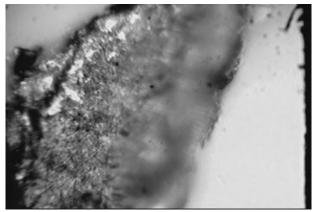


Figure (5.40): Microstructure of commercially pure aluminum after an exposure of 24 hrs to 0.2 M HCl solution at 60°C, at magnification of X400.

Figure (5.41) is a photograph showing the microstructure of commercially pure Al after an exposure of 24 hrs to 0.2 M NaOH solution at 60°C at magnification of X400, showing that the black regions are corroded regions within the matrix, and the grains boundaries are vanished.

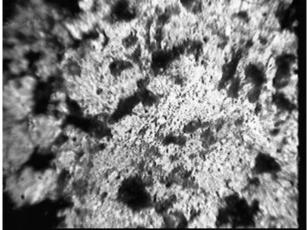


Figure (5.41): Microstructure of commercially pure aluminum after an exposure of 24 hrs to 0.2 M NaOH solution at 60°C, at magnification of X400.

Figure (5.42) is a photograph showing the original microstructure of Al-0.15 % Ti-0.112 % V micro-alloy at magnification of X400. It shows the grain refinement effect of 0.112 wt % vanadium addition. The grains are much finer than those of commercially pure Al (figure 5.39).

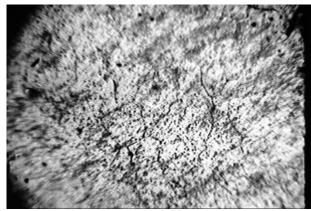


Figure (5.42): Original microstructure of AL-0.15 % Ti-0.112 % V micro alloy, at magnification of X400.

Figures (5.43) and (5.44) are photographs showing the microstructure of Al-0.15 % Ti-0.112 % V micro alloy after an exposure of 24 hrs to 0.2 M HCl and 0.2 M NaOH solutions at 60°C respectively, at magnification of X400. It show that the grains and its boundaries are wiped off, being more pronouncly in NaOH solution, which means higher corrosion rates. This agrees with the results obtained in the previous figures for the corrosion rate of Al in the solutions.

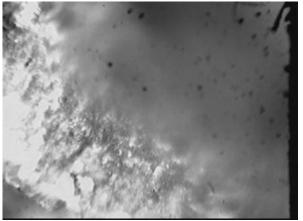


Figure (5.43): Microstructure of AL-0.15 % Ti-0.112 % V micro alloy after an exposure of 24 hrs to 0.2 M HCl solution at 60°C, at magnification of X400.

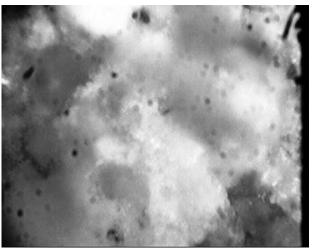


Figure (5.44): Microstructure of AL-0.15 % Ti-0.112 % V micro alloy after an exposure of 24 hrs to 0.2 M NaOH solution at 60°C, at magnification of X400.

# CHAPTER SIX: CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

#### **6.1 Conclusions**

The main conclusions of this work are presented below:

- 1- The increase in temperature increased the corrosion rate of commercially pure Al grain refined by Ti with different V addition. However, based on the results obtained in this thesis the V addition to commercially pure Al grain refined by Ti resulted in improvement of its corrosion resistance in HCl solution at 25, 40 and 60 °C. The maximum improvement was 76.75 % at 0.148 wt % V at 40 °C.
- 2- The presence of NaF inhibitor in HCl solution has resulted in enhancement of the corrosion resistance of commercially pure Al grain refined by different percentage of V addition at 25, 40 and 60 °C. The inhibition efficiency increased by increasing temperature where about 95 % increases was achieved at 60 °C.
- 3- Addition of V to commercially pure Al at any percentage resulted in improvement of its corrosion resistance in NaOH solution at 25, 40 and 60 °C. The maximum improvement was 40.29 % at 0.148 wt % V at 60 °C. The corrosion rate increased with increase of temperature. This was identified by the metal examination of the corroded surfaces.
- 4- The presence of  $K_2Cr_2O_7$  inhibitor in the NaOH solution has resulted in enhancement of the corrosion resistance of commercially pure Al grain refined by different percentage of V addition at 25, 40 and 60 °C. The inhibition efficiency increased by increase of temperature, and the maximum increase in inhibition efficiency was 99.6 % for 0.236 wt % V at 40 °C.

### **6.2 Suggestions for Future Work**

The following points may be suggested for future work:

- 1- The effect of addition of grain refiners e.g. Ti, Ti+B, Mo and Hf to aluminum and investigate their effect on corrosion resistance both in acidic and alkaline solutions.
- 2- Investigation of the effect of the presence of other inhibitors e.g. sodium hexametaphosphate, molybdates and nitrates on the corrosion rate of aluminum in acidic and alkaline solutions.
- 3- The effect of addition of two grain refiners together to aluminum and investigate their effect on its corrosion resistance in acidic and alkaline solutions in the absence or presence of different inhibitors.
- 4- Investigation of the points above at different temperatures.
- 5- The effect of stirring velocity following the experiments adapted in this thesis on the corrosion rate may be investigated.

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APPENDIX (A)

**A1:** Corrosion Rate Calculations

Corrosion rate was calculated using the following equations in HCl and NaOH solutions with and without inhibitor:

1- 
$$CR = \frac{\Delta w}{A \times t}$$
 Eq.(A1.1)

$$A = \pi r^2$$
 ..... Eq.(A1.2)

$$t=24 \text{ hr} \times \frac{1 \text{ day}}{24 \text{ hr}} \times \frac{1 \text{ yr}}{365 \text{ day}} = 2.7397 \times 10^{-3} \text{ yr}$$

Where:

CR: The corrosion rate (mg/mm<sup>2</sup>.yr).

 $\Delta$ W: Weight loss (mg).

t: Time (yr).

A: Surface area exposed to test in the corrosive medium (mm<sup>2</sup>).

As an example, for addition of 0.112 wt % V at 25 °C in 0.2 M HCl solution:

CR (mg/mm<sup>2</sup>.yr)=
$$\frac{(0.00135)\text{mg}}{(\pi \times 4.5^2)\text{mm}^2 \times (2.7397 \times 10^{-3})\text{yr}}$$

$$=7.75 \text{ mg/mm}^2.\text{yr}$$

2- 
$$CR = \frac{\Delta w}{t}$$
 Eq.(A1.3)

Where:

CR: The corrosion rate (mg/yr).

As an example, for addition of 0.112 wt % V at 25  $^{\circ}$ C in 0.2 M HCl solution:

CR (mg/yr) = 
$$\frac{(0.00135)\text{mg}}{(0.0027397)\text{yr}}$$
  
=492.75 mg/yr

A2: Percentage Decrease in the Corrosion Rate up on the Addition of Vanadium as a Grain Refiner Calculation

The percentage decrease in the corrosion rate as a result of adding V as a grain refiner to commercially pure Al in HCl and NaOH solutions is calculated as:

%DCR= 
$$\frac{\text{(Corrosion Rate at 0 \% V-Corrosion Rate at 0.112 \% V)}}{\text{Corrosion Rate at 0 \% V}} \times 100\%$$
.....Eq. (A2.1)

As an example, for addition of 0.112 wt % V at 25 °C in 0.2 M HCl solution:

% DCR=
$$\frac{11.16-7.75}{11.16}$$
×100%

**A3:** Inhibition Efficiency Calculation

The inhibition efficiency ( $\eta$  %) was calculated using the following formula in both HCl and NaOH solutions containing inhibitor:

$$\eta\% = \frac{\text{CR}_b\text{-CR}_{wi}}{\text{CR}_b} \times 100. \text{Eq.(A3.1)}$$

As an example, for addition of 0.112 wt % V in 0.2 M HCl solution in the presence of 4 wt % NaF:

$$\eta\% = \frac{7.75 - 3.16}{7.75} \times 100 \%$$

APPENDIX (B)

**B1:** Effect of Vanadium Addition to Commercially Pure Aluminum Grain Refined by Titanium on the Corrosion Rate in HCl solution at Different Temperatures.

Table (B1.1): Corrosion rate in 0.2 M HCl solution at 25 °C.

Run No. 1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.2163	2.2146	0.0017	0.0767
0.005	2.1241	2.0951	0.029	1.3653
0.053	2.0339	2.0334	0.0005	0.0246
0.112	1.7635	1.7627	0.0008	0.0454
0.148	2.0466	2.0409	0.0057	0.2785
0.236	2.0856	2.0839	0.0017	0.0815

Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.2146	2.2115	0.0031	0.1400
0.005	2.0951	2.0859	0.0092	0.4391
0.053	2.0334	2.028	0.0054	0.2656
0.112	1.7627	1.7608	0.0019	0.1078
0.148	2.0409	2.0402	0.0007	0.0343
0.236	2.0839	2.0823	0.0016	0.0768

V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)
0	0.0017	7.90	620.51
0.005	0.0092	42.78	3358.03
0.053	0.0005	2.32	182.50
0.112	0.0008	4.59	292.00
0.148	0.0007	3.25	255.50
0.236	0.0016	7.44	584.01

V %	max Δ wt (g)	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0031	14.41	1131.51
0.005	0.029	134.84	10585.10
0.053	0.0054	25.11	1971.02
0.112	0.0019	10.91	693.51
0.148	0.0057	26.50	2080.52
0.236	0.0017	7.90	620.51

V %	AVG $\Delta$ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.0024	11.16	876.01
0.005	0.0191	88.81	6971.57
0.053	0.00295	13.72	1076.76
0.112	0.00135	7.75	492.75
0.148	0.0032	14.88	1168.01
0.236	0.00165	7.67	602.26

<u>Table (B1.2)</u>: Corrosion rate in 0.2 M HCl solution at 40  $^{\circ}$ C.

Run No. 1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.2115	2.1986	0.0129	0.5833
0.005	2.0859	2.0420	0.0439	2.1046
0.053	2.0280	2.0275	0.0005	0.0247
0.112	1.7608	1.7579	0.0029	0.1647
0.148	2.0402	2.0394	0.0008	0.0392
0.236	2.0823	2.0776	0.0047	0.2257

Run No. 2				, '
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1910	2.1682	0.0228	1.0406
0.005	2.0159	1.9671	0.0488	2.4208
0.053	2.0223	2.0137	0.0086	0.4253
0.112	1.7543	1.7454	0.0089	0.5073
0.148	2.0337	2.0262	0.0075	0.3688
0.236	2.0753	2.0669	0.0084	0.4048

V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)
0	0.0129	59.98	4708.54
0.005	0.0439	204.12	16023.65
0.053	0.0005	2.32	182.50
0.112	0.0029	16.65	1058.51
0.148	0.0008	3.72	292.00
0.236	0.0047	21.85	1715.52

V %	max Δ wt (g)	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0228	106.01	8322.08
0.005	0.0488	226.91	17812.17
0.053	0.0086	39.99	3139.03
0.112	0.0089	51.09	3248.53
0.148	0.0075	34.87	2737.53
0.236	0.0084	39.06	3066.03

V %	AVG $\Delta$ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.02	83.00	6515.31
0.005	0.05	215.51	16917.91
0.053	0.00	21.16	1660.77
0.112	0.01	33.87	2153.52
0.148	0.00	19.30	1514.76

<u>Table (B1.3)</u>: Corrosion rate in 0.2 M HCl solution at 60  $^{\circ}$ C.

Run No. 1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1695	2.1128	0.0567	2.61
0.005	2.1088	2.0662	0.0426	2.02
0.053	2.0137	1.9741	0.0396	1.97
0.112	1.7454	1.7149	0.0305	1.75
0.148	2.3253	2.2745	0.0508	2.18
0.236	2.0644	2.0392	0.0252	1.22

Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1128	2.0265	0.0863	4.08
0.005	2.0662	1.9812	0.0850	4.11
0.053	1.9741	1.9341	0.0400	2.03
0.112	1.7149	1.6461	0.0688	4.01
0.148	2.2745	2.1937	0.0808	3.55
0.236	2.0392	1.9759	0.0633	3.10

V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)
0	0.0567	263.64	20695.70
0.005	0.0426	198.08	15549.15
0.053	0.0396	184.13	14454.14
0.112	0.0305	175.08	11132.61
0.148	0.0508	236.21	18542.18
0.236	0.0252	117.17	9198.09

V %	max Δ wt (g)	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0863	401.27	31499.80
0.005	0.085	395.23	31025.29
0.053	0.04	185.99	14600.14
0.112	0.0688	394.94	25112.24
0.148	0.0808	375.70	29492.28
0.236	0.0633	294.33	23104.72

V %	AVG Δ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.0715	332.46	26097.75
0.005	0.0638	296.65	23287.22
0.053	0.0398	185.06	14527.14
0.112	0.04965	285.01	18122.42
0.148	0.0658	305.95	24017.23
0.236	0.04425	205.75	16151.40

Table (B1.4): Percentage Decrease in corrosion rate (%DCR) upon the addition of vanadium as a grain refiner in 0.2 M HCl at 25 °C.

V %	% DCR
0.005	-695.83
0.053	-22.92
0.112	30.56
0.148	-33.33
0.236	31.25

Table (B1.5): Percentage Decrease in corrosion rate (%DCR) upon the addition of vanadium as a grain refiner in 0.2 M HCl solution at  $40\,^{\circ}$ C.

V %	% DCR
0.005	-159.66
0.053	74.51
0.112	59.19
0.148	76.75
0.236	63.31

Table (B1.6): Percentage Decrease in corrosion rate (%DCR) upon the addition of vanadium as a grain refiner in 0.2 M HCl solution at 60 °C.

V %	% DCR
0.005	10.77
0.053	44.34
0.112	14.27
0.148	7.97
0.236	38.11

Table (B1.7): Corrosion rate (mg/mm<sup>2</sup>.yr) in 0.2 M HCl solution at 25, 40 and 60°C.

V %	CR (mg/mm <sup>2</sup> .yr) at 25 °C	CR (mg/mm <sup>2</sup> .yr) at 40 °C	CR (mg/mm <sup>2</sup> .yr) at 60 °C
0	11.16	83.00	332.46
0.005	88.81	215.51	296.65
0.053	13.72	21.16	185.06
0.112	7.75	33.87	285.01
0.148	14.88	19.30	305.95
0.236	7.67	30.46	205.75

Table (B1.8): Corrosion rate (mg/yr) in 0.2 M HCl solution at 25, 40 and 60°C.

V %	CR (mg/yr) at 25 °C	CR (mg/yr) at 40 °C	CR (mg/yr) at 60 °C
0	876.01	6515.31	26097.75
0.005	6971.57	16917.91	23287.22
0.053	1076.76	1660.77	14527.14
0.112	492.75	2153.52	18122.42
0.148	1168.01	1514.76	24017.23
0.236	602.26	2390.77	16151.40

B2: Effect of Vanadium Addition to Commercially Pure Aluminum Grain Refined by Titanium on the Corrosion Rate in HCl solution in the Presence of NaF as an Inhibitor at Different Temperatures.

Table (B2.1): Corrosion rate in 0.2 M HCl solution in the presence of 4 wt % NaF as an inhibitor at 25  $^{\rm o}C.$ 

Run No.1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1997	2.1980	0.0017	0.0773
0.005	2.1311	2.1307	0.0004	0.0188
0.053	2.0219	2.0211	0.0008	0.0396
0.112	2.0039	2.0033	0.0006	0.0299
0.148	2.3526	2.3519	0.0007	0.0298
0.236	2.0882	2.0878	0.0004	0.0192

Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1980	2.1961	0.0019	0.0864
0.005	2.1307	2.1289	0.0018	0.0845
0.053	2.0211	2.0202	0.0009	0.0445
0.112	2.0033	2.0028	0.0005	0.0250
0.148	2.3519	2.3511	0.0008	0.0340
0.236	2.0878	2.0873	0.0005	0.0239

V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)
0	0.0017	7.90	620.51
0.005	0.0004	1.86	146.00
0.053	0.0008	3.72	292.00
0.112	0.0005	2.87	182.50
0.148	0.0007	3.25	255.50
0.236	0.0004	1.86	146.00

V %	$\max \Delta \operatorname{wt}(g)$	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0019	8.83	693.51
0.005	0.0018	8.37	657.01
0.053	0.0009	4.18	328.50
0.112	0.0006	3.44	219.00
0.148	0.0008	3.72	292.00
0.236	0.0005	2.32	182.50

V %	AVG $\Delta$ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.0018	8.37	657.01
0.005	0.0011	5.11	401.50
0.053	0.00085	3.95	310.25
0.112	0.00055	3.16	200.75
0.148	0.00075	3.49	273.75
0.236	0.00045	2.09	164.25

Table (B2.2): Corrosion rate in 0.2 M HCl solution in the presence of 4 wt % NaF as an inhibitor at 40  $^{\rm o}C.$ 

Run No. 1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	%Error
0	2.1915	2.1894	0.0021	0.0958
0.005	2.1253	2.1243	0.001	0.0471
0.053	2.017	2.0146	0.0024	0.1190
0.112	1.9967	1.9961	0.0006	0.0300
0.148	2.3465	2.3447	0.0018	0.0767
0.236	2.0809	2.0794	0.0015	0.0721

Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	Δ wt (g)	% Error
0	2.1894	2.183	0.0064	0.2923
0.005	2.1243	2.1213	0.003	0.1412
0.053	2.0146	2.0125	0.0021	0.1042
0.112	1.9961	1.9934	0.0027	0.1353
0.148	2.3447	2.3426	0.0021	0.0896
0.236	2.0794	2.0771	0.0023	0.1106
V %	min $\Delta$ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)	
0	0.0021	9.76	766.51	
0.005	0.001	4.65	365.00	
0.053	0.0021	9.76	766.51	
0.112	0.0006	3.44	219.00	
0.148	0.0018	8.37	657.01	
0.236	0.0015	6.97	547 51	

V %	max Δ wt (g)	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0064	29.76	2336.02
0.005	0.003	13.95	1095.01
0.053	0.0024	11.16	876.01
0.112	0.0027	15.50	985.51
0.148	0.0021	9.76	766.51
0.236	0.0023	10.69	839.51

V %	AVG Δ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.00425	19.76	1551.26
0.005	0.002	9.30	730.01
0.053	0.00225	10.46	821.26
0.112	0.00165	9.47	602.26
0.148	0.00195	9.07	711.76
0.236	0.0019	8.83	693.51

Table (B2.3): Corrosion rate in 0.2 M HCl solution in the presence of 4 wt % NaF as an inhibitor at 60  $^{\rm o}C.$ 

Run No. 1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.183	2.1781	0.0049	0.2245
0.005	2.1213	2.1184	0.0029	0.1367
0.053	2.0125	2.0067	0.0058	0.2882
0.112	1.9934	1.9898	0.0036	0.1806
0.148	2.3426	2.3364	0.0062	0.2647
0.236	2.0771	2.0750	0.0021	0.1011

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Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1781	2.1741	0.004	0.1836
0.005	2.1184	2.1144	0.004	0.1888
0.053	2.0067	2.0013	0.0054	0.2691
0.112	1.9898	1.9864	0.0034	0.1709
0.148	2.3364	2.3343	0.0021	0.0899
0.236	2.0750	2.0712	0.0038	0.1831
V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)	
0	0.004	18.60	1460.01	
0.005	0.0029	13.48	1058.51	
0.053	0.0054	25.11	1971.02	
0.112	0.0034	19.52	1241.01	
0.148	0.0021	9.76	766.51	
0.236	0.0021	9.76	766.51	

V %	max Δ wt (g)	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0049	22.78	1788.52
0.005	0.004	18.60	1460.01
0.053	0.0058	26.97	2117.02
0.112	0.0036	20.67	1314.01
0.148	0.0062	28.83	2263.02
0.236	0.0038	17.67	1387.01

V %	AVG $\Delta$ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.00445	20.69	1624.27
0.005	0.00345	16.04	1259.26
0.053	0.0056	26.04	2044.02
0.112	0.0035	20.09	1277.51
0.148	0.00415	19.30	1514.76
0.236	0.00295	13.72	1076.76

Table (B2.4): Corrosion rate (mg/mm $^2$ .yr) in 0.2 M HCl solution in the presence of 4 wt % NaF as an inhibitor at 25, 40 and 60  $^{\circ}$ C.

V %	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr) at 25 °C	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr) at 40 °C	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr) at 60 °C
0	8.37	19.76	20.69
0.005	5.11	9.30	16.04
0.053	3.95	10.46	26.04
0.112	3.16	9.47	20.09
0.148	3.49	9.07	19.30
0.236	2.09	8.83	13.72

Table (B2.5): Corrosion rate (mg/yr) in 0.2 M HCl solution in the presence of 4 wt % NaF as an inhibitor at 25, 40 and 60  $^{\circ}$ C.

V %	CR <sub>wi</sub> (mg/yr) at 25 °C	CR <sub>wi</sub> (mg/yr) at 40 °C	CR <sub>wi</sub> (mg/yr) at 60 °C
0	657.01	1551.26	1624.27
0.005	401.50	730.01	1259.26
0.053	310.25	821.26	2044.02
0.112	200.75	602.26	1277.51
0.148	273.75	711.76	1514.76
0.236	164.25	693.51	1076.76

**B3:** Effect of Vanadium Addition to Commercially Pure Aluminum Grain Refined by Titanium on the Corrosion Rate in NaOH Solution at Different Temperatures.

<u>Table (B3.1): Corrosion rate in 0.2 M NaOH solution at 25  $^{\circ}$ C.</u>

Run No. 1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.0075	2.0023	0.0052	0.2590
0.005	1.5545	1.546	0.0085	0.5468
0.053	1.6216	1.6195	0.0021	0.1295
0.112	1.4351	1.4329	0.0022	0.1533
0.148	1.5521	1.5478	0.0043	0.2770
0.236	1.6155	1.6120	0.0035	0.2167

Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.0023	1.9985	0.0038	0.1898
0.005	1.546	1.5381	0.0079	0.5110
0.053	1.6195	1.616	0.0035	0.2161
0.112	1.4329	1.4303	0.0026	0.1815
0.148	1.5478	1.5441	0.0037	0.2390
0.236	1.6120	1.6091	0.0029	0.1799

V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)
0	0.0038	17.67	1387.01
0.005	0.0079	36.73	2883.53
0.053	0.0021	9.76	766.51
0.112	0.0022	12.63	803.01
0.148	0.0037	17.20	1350.51
0.236	0.0029	13.48	1058.51

V %	max Δ wt (g)	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0052	24.18	1898.02
0.005	0.0085	39.52	3102.53
0.053	0.0035	16.27	1277.51
0.112	0.0026	14.93	949.01
0.148	0.0043	19.99	1569.51
0.236	0.0035	16.27	1277.51

V %	AVG $\Delta$ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.0045	20.92	1642.52
0.005	0.0082	38.13	2993.03
0.053	0.0028	13.02	1022.01
0.112	0.0024	13.78	876.01
0.148	0.004	18.60	1460.01
0.236	0.0032	14.88	1168.01

<u>Table (B3.2)</u>: Corrosion rate in 0.2 M NaOH solution at 40  $^{\circ}$ C.

Run No. 1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	1.9934	1.967	0.0264	1.3244
0.005	1.5167	1.4627	0.054	3.5604
0.053	1.5772	1.5375	0.0397	2.5171
0.112	1.3084	1.2887	0.0197	1.5057
0.148	1.4865	1.4414	0.0451	3.0340
0.236	1.5106	1.4893	0.0213	1.4100

Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	1.967	1.9299	0.0371	1.8861
0.005	1.4627	1.402	0.0607	4.1499
0.053	1.5375	1.5169	0.0206	1.3398
0.112	1.2887	1.263	0.0257	1.9943
0.148	1.4414	1.4083	0.0331	2.2964
0.236	1.4893	1.4605	0.0288	1.9338

V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)
0	0.0264	122.75	9636.09
0.005	0.054	251.09	19710.19
0.053	0.0206	95.78	7519.07
0.112	0.0197	91.60	7190.57
0.148	0.0331	153.91	12081.61
0.236	0.0213	99.04	7774.57

V %	$\max \Delta wt(g)$	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0371	172.50	13541.63
0.005	0.0607	282.24	22155.71
0.053	0.0397	184.59	14490.64
0.112	0.0257	147.53	9380.59
0.148	0.0451	209.70	16461.66
0.236	0.0288	133.91	10512.10

V %	AVG Δ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.03175	147.63	11588.86
0.005	0.05735	266.66	20932.95
0.053	0.03015	140.19	11004.85
0.112	0.0227	130.31	8285.58
0.148	0.0391	181.80	14271.64
0.236	0.02505	116.48	9143.34

<u>Table (B3.3)</u>: Corrosion rate in 0.2 M NaOH solution at 60  $^{\circ}$ C.

Run No. 1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	1.8941	1.8052	0.0889	4.6935
0.005	1.9506	1.8635	0.0871	4.4653
0.053	1.1261	1.058	0.0681	6.0474
0.112	0.8659	0.8162	0.0497	5.7397
0.148	1.1826	1.1148	0.0678	5.7331
0.236	1.0891	1.0378	0.0513	4.7103

Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	1.8052	1.7437	0.0615	3.4068
0.005	1.8635	1.7641	0.0994	5.3340
0.053	1.058	1.0007	0.0573	5.4159
0.112	0.8162	0.7761	0.0401	4.9130
0.148	1.1148	1.0413	0.0735	6.5931
0.236	1.0378	0.9791	0.0587	5.6562

V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)
0	0.0615	285.96	22447.71
0.005	0.0871	404.99	31791.80
0.053	0.0573	266.43	20914.70
0.112	0.0401	230.19	14636.64
0.148	0.0678	315.25	24747.24
0.236	0.0513	238.53	18724.68

V %	max Δ wt (g)	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0889	413.36	32448.81
0.005	0.0994	462.18	36281.34
0.053	0.0681	316.65	24856.74
0.112	0.0497	285.30	18140.67
0.148	0.0753	350.12	27484.76
0.236	0.0587	272.94	21425.70

V %	AVG Δ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.0752	349.66	27448.26
0.005	0.09325	433.59	34036.57
0.053	0.0627	291.54	22885.72
0.112	0.0449	257.74	16388.66
0.148	0.07065	328.50	25787.49
0.236	0.055	255.73	20075.19

Table (B3.4): Percentage Decrease in corrosion rate (%DCR) upon the addition of vanadium as a grain refiner in 0.2 M NaOH at 25 °C.

V %	% DCR
0.005	-82.22
0.053	37.78
0.112	34.16
0.148	11.11
0.236	28.89

Table (B3.5): Percentage Decrease in corrosion rate (%DCR) upon the addition of vanadium as a grain refiner in 0.2 M NaOH at 40 °C.

V %	% DCR
0.005	-80.63
0.053	5.04
0.112	28.50
0.148	-23.15
0.236	21.10

Table (B3.6): Percentage Decrease in corrosion rate (%DCR) upon the addition of vanadium as a grain refiner in 0.2 M NaOH at 60 °C.

V %	% DCR
0.005	-24.00
0.053	16.62
0.112	40.29
0.148	6.05
0.236	26.86

Table (B3.7): Corrosion rate (mg/mm<sup>2</sup>.yr) in 0.2 M NaOH solution at 25, 40 and 60 °C.

V %	CR (mg/mm <sup>2</sup> .yr) at 25 °C	CR (mg/mm <sup>2</sup> .yr) at 40 °C	CR (mg/mm <sup>2</sup> .yr) at 60 °C
0	20.92	147.63	349.66
0.005	38.13	266.66	433.59
0.053	13.02	140.19	291.54
0.112	13.78	130.31	257.74
0.148	18.60	181.80	328.50
0.236	14.88	116.48	255.73

Table (B3.8): Corrosion rate (mg/yr) in 0.2 M NaOH solution at 25, 40 and 60 °C.

V %	CR (mg/yr) at 25 °C	CR (mg/yr) at 40 °C	CR (mg/yr) at 60 °C
0	1642.52	11588.86	27448.26
0.005	2993.03	20932.95	34036.57
0.053	1022.01	11004.85	22885.72
0.112	876.01	8285.58	16388.66
0.148	1460.01	14271.64	25787.49
0.236	1168.01	9143.34	20075.19

B4: Effect of Vanadium Addition to Commercially Pure Aluminum Grain Refined by Titanium on the Corrosion Rate in NaOH in the Presence of  $K_2Cr_2O_7$  as an Inhibitor at Different Temperatures.

Table (B4.1): Corrosion rate in 0.2 M NaOH solution in the presence of 3 wt %  $\underline{K_2Cr_2O_7}$  as an inhibitor at 25 °C.

wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
2.172	2.1714	0.0006	0.0276
2.1126	2.1119	0.0007	0.0331
1.9992	1.9977	0.0015	0.0750
1.9843	1.9829	0.0014	0.0706
2.3322	2.3304	0.0018	0.0772
2.0691	2.0676	0.0015	0.0725
	2.172 2.1126 1.9992 1.9843 2.3322	2.172     2.1714       2.1126     2.1119       1.9992     1.9977       1.9843     1.9829       2.3322     2.3304	2.172     2.1714     0.0006       2.1126     2.1119     0.0007       1.9992     1.9977     0.0015       1.9843     1.9829     0.0014       2.3322     2.3304     0.0018

Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1714	2.1711	0.0003	0.0138
0.005	2.1119	2.1114	0.0005	0.0237
0.053	1.9977	1.9964	0.0013	0.0651
0.112	1.9829	1.9816	0.0013	0.0656
0.148	2.3304	2.3288	0.0016	0.0687
0.236	2.0676	2.0661	0.0015	0.0725

V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)
0	0.0003	1.39	109.50
0.005	0.0005	2.32	182.50
0.053	0.0013	6.04	474.50
0.112	0.0013	7.46	474.50
0.148	0.0016	7.44	584.01
0.236	0.0015	6.97	547.51

V %	max Δ wt (g)	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0006	2.79	219.00
0.005	0.0007	3.25	255.50
0.053	0.0015	6.97	547.51
0.112	0.0014	8.04	511.00
0.148	0.0018	8.37	657.01
0.236	0.0015	6.97	547.51

V %	AVG Δ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.00045	2.09	164.25
0.005	0.0006	2.79	219.00
0.053	0.0014	6.51	511.00
0.112	0.00135	7.75	492.75
0.148	0.0017	7.90	620.51
0.236	0.0015	6.97	547.51

Table (B4.2): Corrosion rate in 0.2 M NaOH solution in the presence of 3 wt %  $K_2Cr_2O_7$  as an inhibitor at 40  $^{\rm o}C.$ 

Run No. 1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1711	2.1707	0.0004	0.0184
0.005	2.1114	2.1102	0.0012	0.0568
0.053	1.9964	1.9953	0.0011	0.0551
0.112	1.9816	1.9810	0.0006	0.0303
0.148	2.3288	2.3280	0.0008	0.0344
0.236	2.0661	2.0660	0.0001	0.0048

Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1707	2.1702	0.0005	0.0230
0.005	2.1102	2.1100	0.0002	0.0095
0.053	1.9953	1.9945	0.0008	0.0401
0.112	1.9810	1.9802	0.0008	0.0404
0.148	2.3280	2.3275	0.0005	0.0215
0.236	2.0660	2.0659	0.0001	0.0048

V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)
0	0.0004	1.86	146.00
0.005	0.0002	0.93	73.00
0.053	0.0008	3.72	292.00
0.112	0.0006	3.44	219.00
0.148	0.0005	2.32	182.50
0.236	0.0001	0.46	36.50

V %	max Δ wt (g)	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0005	2.32	182.50
0.005	0.0012	5.58	438.00
0.053	0.0011	5.11	401.50
0.112	0.0008	4.59	292.00
0.148	0.0008	3.72	292.00
0.236	0.0001	0.46	36.50

V %	AVG Δ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.00045	2.09	164.25
0.005	0.00070	3.25	255.50
0.053	0.00095	4.42	346.75
0.112	0.00070	4.02	255.50
0.148	0.00065	3.02	237.25
0.236	0.00010	0.46	36.50

Table (B4.3): Corrosion rate in 0.2 M NaOH solution in the presence of 3 wt %  $\underline{K_2Cr_2O_7}$  as an inhibitor at 60 °C.

Run No. 1				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1702	2.1698	0.0004	0.0184
0.005	2.11	2.109	0.001	0.0474
0.053	1.9945	1.9941	0.0004	0.0201
0.112	1.9802	1.9796	0.0006	0.0303
0.148	2.3275	2.3265	0.001	0.0430
0.236	2.0659	2.065	0.0009	0.0436

Run No. 2				
V %	wt (g)at 0 time	wt (g) after 24 hrs	$\Delta$ wt (g)	% Error
0	2.1698	2.1695	0.0003	0.0138
0.005	2.109	2.1088	0.0002	0.0095
0.053	1.9941	1.9931	0.001	0.0501
0.112	1.9796	1.9788	0.0008	0.0404
0.148	2.3265	2.3253	0.0012	0.0516
0.236	2.065	2.0644	0.0006	0.0291

V %	min Δ wt (g)	CR <sub>min</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>min</sub> (mg/yr)
0	0.0003	1.39	109.50
0.005	0.0002	0.93	73.00
0.053	0.0004	1.86	146.00
0.112	0.0006	3.44	219.00
0.148	0.0010	4.65	365.00
0.236	0.0006	2.79	219.00

V %	max Δ wt (g)	CR <sub>max</sub> (mg/mm <sup>2</sup> .yr)	CR <sub>max</sub> (mg/yr)
0	0.0004	1.86	146.00
0.005	0.0010	4.65	365.00
0.053	0.0010	4.65	365.00
0.112	0.0008	4.59	292.00
0.148	0.0012	5.58	438.00
0.236	0.0009	4.18	328.50

V %	AVG $\Delta$ wt (g)	CR (mg/mm <sup>2</sup> .yr)	CR (mg/yr)
0	0.00035	1.63	127.75
0.005	0.00060	2.79	219.00
0.053	0.00070	3.25	255.50
0.112	0.00070	4.02	255.50
0.148	0.00110	5.11	401.50
0.236	0.00075	3.49	273.75

Table (B4.4): Corrosion rate (mg/mm $^2$ .yr) in 0.2 M NaOH solution in the presence of 3 wt %  $K_2Cr_2O_7$  as an inhibitor at 25, 40 and 60  $^{\circ}C$ .

% V	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr) at 25 °C	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr) at 40 °C	CR <sub>wi</sub> (mg/mm <sup>2</sup> .yr) at 60 °c
0	2.09	2.09	1.63
0.005	2.79	3.25	2.79
0.053	6.51	4.42	3.25
0.112	7.75	4.02	4.02
0.148	7.90	3.02	5.11
0.236	6.97	0.46	3.49

Table (B4.5): Corrosion rate (mg/yr) in 0.2 M NaOH solution in the presence of 3 wt %  $K_2Cr_2O_7$  as an inhibitor at 25, 40 and 60  $^{\circ}C$ .

% V	CR <sub>wi</sub> (mg/yr) at 25 °C	CR <sub>wi</sub> (mg/yr) at 40 °C	CRwi(mg/yr) at 60 °c
0	164.25	164.25	127.75
0.005	219.00	255.50	219.00
0.053	511.00	346.75	255.50
0.112	492.75	255.50	255.50
0.148	620.51	237.25	401.50
0.236	547.51	36.50	273.75

## تأثير إضافة الفاناديوم على مقاومة التآكل الكيميائي للألمنيوم النقي تجاريا والمنعم بالتيتانيوم عند درجات حرارة مختلفة

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## ملخص

يتجمد مصهور الألمنيوم وسبائكه مكونا تركيبا عموديا ذو حبيبات كبيرة و خشنة . لذا يتم تنعيم الألمنيوم من قبل عناصر مختلفة مثل التيتانيوم و التيتانيوم زائدا البورون ، و قد بدأ العمل بهذه الطريقه منذ منتصف الخمسينات لإنتاج هيكل منعم و متجانس من سبائك الألمنيوم ، و لقعزيز خصائصه الميكانيكية و نوعية سطحه.

وعلى الرغم من أن تأثير التنعيم على خواص المواد و السلوك الميكانيكي قد تمت دراسته و توثيقه، إلا أن تأثيره على سلوك التآكل للمعدن في الأوساط الكيميائية عند ظروف تشغيل مختلفة نادرا ما تمت دراسته.

في هذه الأطروحة، تمت دراسة تأثير إضافة نسب أوزان مختلفة من الفاناديوم على مقاومة التآكل الكيميائي للألمنيوم النقي تجاريا والمنعم بالتيتانيوم في المحاليل الحمضية و القاعدية بدون ومع مثبط عند ثلاث درجات حرارة مختلفة.

وخلصة الدراسة إلى أن الزيادة في درجات الحرارة أدت إلى زيادة معدل التآكل للألمنيوم النقي تجاريا المنعّم بالتيتانيوم والمنعّم بنسب أوزان مختلفة من الفاناديوم في كل من محلول حمض الهيدروكلوريك (0.2) مول/لتر).

كما وجد أن إضافة الفاناديوم عند أي نسبة مئوية إلى الألمنيوم النقي تجاريا و المنعم بالتيتانيوم أدت إلى تحسين مقاومته للتآكل في كل من محلول حمض الهيدروكلوريك و هيدروكسيد الصوديوم عند درجات الحرارة الثلاثة: 25، 40 و 60 درجة مئوية. وكان أقصى تحسين في حمض الهيدروكلوريك 76.75 % عند 0.148 % فاناديوم و 40 درجة مئوية ، أما في هيدروكسيد الصوديوم فكانت 40.29 % عند 40.18 % فاناديوم و 60 درجة مئوية. وألكنت هذه النتائج مع الصور المجهرية العامة للعينات المتآكلة في كل من محلول حمض الهيدروكلوريك و هيدروكسيد الصوديوم.

في حالة وجود 4 % كنسبة وزنية من فلوريد الصوديوم كمثبط في محلول حمض الهيدروكلوريك و 3 % كنسبة وزنية من ثاني كرومات البوتاسيوم في محلول هيدروكسيد الصوديوم، أدى ذلك إلى تعزين مقاومة التآكل في الألمنيوم النقي تجاريا المنعم بالتيتانيوم و المضاف إليه نسب أوزان مختلفة من الفاناديوم عند درجات الحرارة المختلفة التي تمت دراستها.

وأخيرا تبين أنه زيادة كفاءة التثبيط تزداد بإزدياد درجة الحرارة، حيث تم الهصرول على حوالي 95.6 % عند 0.005 % فاناديوم و 40 درجة مئوية في محلول حمض الهيدروكلوريك كزيادة قصوى ، وإلى حوالي 99.6 % عند 0.236 % فاناديوم و 40 درجة مئوية في محلول هيدروكسيد الصوديوم.